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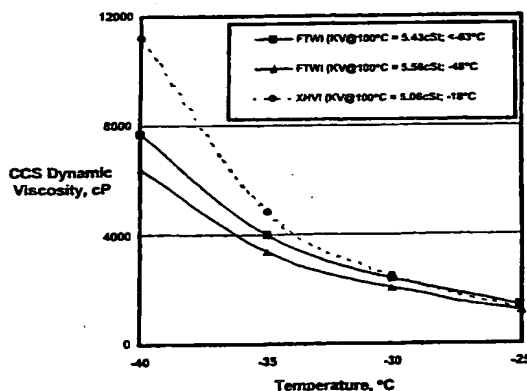
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(54) Title: FORMULATED LUBRICANT OILS CONTAINING HIGH-PERFORMANCE BASE OILS DERIVED FROM  
HIGHLY PARAFFINIC HYDROCARBONS

Low-Temperature CCS Viscosity Comparison



(57) Abstract: The present invention relates to formulated lubricant oils derived from a highly paraffinic basestock. The formulated lubricant oils of the present invention comprise a wax isomerate paraffinic hydrocarbon basestock component in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ( $\text{CH}_2 > 4$ ), are such that: (a)  $\text{BI} - 0.5(\text{CH}_2 > 4)15$ ; and (b)  $\text{BI} + 0.85(\text{CH}_2 < 4)5$ ; as measured over the hydrocarbon basestock as a whole. Preferably, the wax isomerate basestocks to be used in the lubricating oils of the present invention have a biodegradability value of at least 50 % under OECD 301 B test. In addition, these basestock components have pour points of about  $-25^\circ\text{C}$  or lower. They are also characterized by unexpectedly good low-temperature and high-temperature viscosities, with CCS viscosity at  $-15^\circ\text{C}$  of not more than about 3 500 cP, and with a kinematic viscosity at  $100^\circ\text{C}$  of about 5 cSt or greater. Desirable multigraded oils obtained using these basestocks may include 0W-, 5W-, 10W-, and 15W-XX grades (XX=20-60).

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FORMULATED LUBRICANT OILS CONTAINING HIGH-PERFORMANCE  
BASE OILS DERIVED FROM HIGHLY PARAFFINIC HYDROCARBONS

FIELD OF THE INVENTION

The present invention relates to formulated lubricant oils possessing a combination of excellent low temperature performance and biodegradability.

BACKGROUND OF THE INVENTION

High performance formulated lubricants depend heavily on the performance characteristics of component base oils (or basestocks) used in blending such products. One traditional problem regarding lubricant oil performance is that of achieving a useable balance of both low-temperature and high-temperature properties. For example, modern multigrade engine oils demand significant performance both at low temperature (for cold engine starts and oil pumpability) as well as at high temperature (viscosity retention, resistance to oxidation and thermal degradation). The trend to SAE "0W" grade engine oils, for example, which require superior low temperature flow properties, increases the demand for lubricants having improved combination of low-temperature and high-temperature performance.

Indeed, the viscosity-temperature relationship of the oil is one of the critical criteria which must be considered when selecting a lubricant for a particular application. For example, the viscosity requirements for qualifications as multi-grade engine oils are described by the SAE Engine Oil Viscosity Classification-SAE J300. These standards apply to both passenger care engine oils (PCEO) and commercial engine oils (CEO). The high-temperature (100°C) viscosity is measured according to ASTM D445, Method of Test for Kinematic

Viscosity of Transparent and Opaque Liquids, and the results are reported in centistokes (cSt). The HTHS viscosity, or high-temperature (150°C) high-shear ( $10^6 \text{ s}^{-1}$ ) viscosity, is measured according to ASTM D4683, Test Method for Measuring Viscosity at High Temperature and High Shear Rate by Tapered Bearing Simulator, and the results are reported in centipoise (cP). The low-temperature (W) viscosity requirements are determined by ASTM D 5293, Method of Test for Apparent Viscosity of Motor Oils at Low Temperature Using the Cold Cranking Simulator (CCS), and the results are reported in centipoise (cP). A second low-temperature viscosity requirement, simulating low-temperature pumping conditions, is determined by MRV (mini rotary viscometer), ASTM D4684, Method for Determination of Yield Stress and Apparent Viscosity of Engine Oils at Low Temperature, with yield stress reported in pascals (Pa) and viscosity reported in centipoise (cP). In addition, a low-temperature pumpability requirement is imposed on multigrade oils, as determined by MRV. It should be noted that CCS viscosity (measured under high energy, high shear conditions) and MRV viscosity (measured under low energy, low shear conditions) are different low-temperature physical properties of lube base oils, and each measures a different characteristic of lube waxiness. Formulated passenger car engine oils must simultaneously meet both critical low-temperature properties of CCS viscosity and MRV viscosity. Table 1 (below) outlines the high- and low-temperature requirements for the recognized SAE grades for engine oils.

Table 1  
Engine Oil Viscosity Grade Specifications (SAE J300)

SAE Grade	<u>Low-Temperature Viscosities</u>		<u>High-Temperature Viscosities</u>		
	CCS	MRV	Kinematic		HTHS
	Viscosity	Viscosity	Viscosity at		Viscosity
	(cP)	(cP)	100°C (cSt)		(cP)
			Min	Max.	
0 W	3250 at -30°C	60000 at -40°C	3.8		
5 W	3500 at -25°C	60000 at -35°C	3.8		
10 W	3500 at -20°C	60000 at -30°C	4.1		
15 W	3500 at -15°C	60000 at -25°C	5.6		
20 W	4500 at -10°C	60000 at -20°C	5.6		
25 W	6000 at -5°C	60000 at -15°C	9.3		
20			5.6	<9.3	2.6 min
30			9.3	<12.5	2.9 min
40			12.5	<16.3	2.9 min (PCEO)
40			12.5	<16.3	3.7 min (CEO)
50			16.3	<21.9	3.7 min
60			21.9	<26.1	3.7 min

The SAE J300 viscosity grades as well as viscosity grades reaching lower or higher than those defined by SAE J300 are encompassed by this specification.

In a similar manner, SAE J306c describes the viscometric qualifications for axle and manual transmission lubricants. High temperature (100°C) viscosity measurements are performed according to ASTM D445. The low temperature viscosity values are determined according to ASTM D2983, Method of Test for Apparent Viscosity at Low Temperature Using the Brookfield Viscometer and these results are reported in centipoise (cP). Table 2 summarizes the high- and low-temperature requirements for qualification of axle and manual transmission lubricants.

Table 2  
Axle/Transmission Oil Viscosity Specifications

SAE Viscosity Grade	Maximum Temperature for Viscosity of 150,000 cP (°C)	Kinematic Viscosity at 100°C (cSt)	
		Min.	Max.
70 W	-55	-	
75 W	-40	4.1	
80 W	-26	7.0	
85 W	-12	11.0	
90	-	13.5	24.0
140	-	24.0	41.0
250	-		

In addition to the viscosity temperature relationship, other properties are, of course, required for an engine oil including, but not limited to, resistance to oxidation under the high temperatures encountered in the engine, resistance to hydrolysis in the presence of the water produced as a combustion product (which may enter the lubricating circulation system as a result of ring blow-by), and since the finished oil is a combination of basestock together with additives, these properties should inhere in all of the components of the oil so that the final, finished lubricant possesses the desired balance of properties over its useful life.

High performance lubricant products with the desired range of low-temperature and high-temperature performance properties may be achieved by formulating with synthetic base oils, including polyalphaolefins (PAO). Synthetic base oils such as PAO are highly advantageous in formulating high-performance lubricants, with desirable low-temperature and high-temperature performance properties. In particular, PAO have especially exhibited excellent low-temperature performance due to its chemical structure and to a composition which contains no waxy hydrocarbon components. One problem with PAO fluids, however, is that they are generally resistant to easy biodegradation due to

their chemical structure. In the event of a release, lubricating oils, including engine oils, gear oils, and transmission oils, may persist long enough to disturb the natural state of the environment. Having high rates of biodegradation is advantageous in the event of such a lubricant release into the environment.

Finished lubricants may also be formulated with high-quality hydro-processed base oils. Hydroprocessed base oils, however, have traditionally demonstrated poorer low-temperature properties and performance than synthetic base oils such as PAO. Accordingly, lube products formulated with hydro-processed base oils have had problems in achieving the low-temperature performance of lube products formulated with PAO base oils. On the other hand, certain hydroprocessed base oils have demonstrated good biodegradability, especially when compared to that of synthetic base oils like PAO.

WO 97/21788 discloses biodegradable hydroprocessed base oils with pour points of  $-15^{\circ}\text{C}$  to  $-24^{\circ}\text{C}$ , with 6.0-7.5 methyl branches per 100 carbons for a hydrocarbon fraction with a boiling point above  $700^{\circ}\text{F}$ , and with 6.8-7.8 methyl branches per 100 carbons for a typical 100N base oil.

U.S. Patent No. 5,366,658 discloses biodegradable base oils for lubricants and functional fluids comprising polymethylalkanes, having terminal methyl groups and having methylene and ethylidene groups. Because of the highly specific synthesis schemes used in making these polymeric fluids, the structure of the polymethylalkanes is highly constrained with branches along the hydrocarbon polymer backbone being exclusively single-carbon ( $\text{C}_1$ ) methyl groups. This structure type is different from that possessed by the wax isomerate fluids, in which the branching groups along the long-chain hydrocarbon backbone include not only methyl ( $\text{C}_1$ ) but also ethyl ( $\text{C}_2$ ), propyl ( $\text{C}_3$ ), butyl ( $\text{C}_4$ ), and possibly other longer hydrocarbon groups. Such mixtures of branching groups,

with differing chain lengths/sizes, impart performance characteristics to long-chain hydrocarbons that are different from the performance features imparted by only methyl ( $C_1$ ) branches.

U.S. Patent No. 5,595,966 and EP 0468109A1 both disclose substantially biodegradable hydrogenated polyalphaolefin (PAO) fluids, which demonstrate from 20% and to at least 40% biodegradation in the CEC L-33-T-82 test. EP 0558835A1 discloses substantially biodegradable unhydrogenated PAO fluids, which demonstrate from 20% to at least 50% biodegradation in the CEC L-33-T-82 test. The PAO's of these references have a chemical structure consisting of a short-to-moderate chain length hydrocarbon backbone with only a few long-chain pendant groups attached.

Normally, a finished lubricant will contain several lubricant components, both base oil(s) and performance additive(s), in order, for example, to achieve desired performance requirements. The development of a balanced lubricant formulation involves considerably more work than the casual use of performance additive(s) in combination with base oil(s). Quite often, functional difficulties may arise from combinations of these materials with certain base oils during actual operating conditions, and unpredictable antagonistic or synergistic effects may become evident. Thus, obtaining suitable formulations require extensive testing and experimentation. Likewise, subtle features of a base oil's chemical composition may significantly influence a base oil's performance in a formulated lubricant. Therefore, matching base oil technology with additive technology is not a routine exercise.

It has now been discovered that certain wax-isomerase basestocks of the present invention demonstrate unusually good low-temperature and high-temperature properties which allow unusually broad formulation flexibility

compared to traditional hydroprocessed base oils. For example, these formulated wax-isomerate type lubricants can meet the extremely stringent viscosity requirements of SAE "0W", particularly SAE 0W-40 crossgraded engine oils, whereas typical hydroprocessed oils with compositions outside the defined compositional range of the present invention cannot reach such a wide crossgrade. Achieving SAE "0W-XX" crossgrades (e.g. XX = 20, 30, 40, 50, 60) is of particular utility because such lubricant formulations are known to have improved fuel economy performance over comparable 5W-XX and higher "W" viscosity grades. Such formulation flexibility at both low and high temperatures is typical of premium synthetic PAO basestocks. In addition, the wax-isomerate derived base oils of this invention unexpectedly demonstrate very good biodegradability, especially when compared to PAO base oils.

#### SUMMARY OF THE INVENTION

In accordance with the present invention, it has now been found that certain wax isomerate basestocks with unexpectedly good biodegradability and viscometric characteristics may be combined with other suitable lubricating oil components to yield fully formulated, biodegradable, multigrade lubricating oils. The performance characteristics of such formulated lubricant products are unexpected, combining the biodegradability typically expected of hydroprocessed lubricants (but not of PAO-type oils) with the wide temperature performance range typically expected of PAO-type lubricants (but not that of conventional hydroprocessed oils).

The formulated lubricant oils of the present invention comprise a wax isomerate paraffinic hydrocarbon basestock component in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene



carbons which are four or more carbons removed from an end group or branch ( $\text{CH}_2>4$ ), are such that:

- (a)  $\text{BI} - 0.5(\text{CH}_2>4) > 15$ ; and
- (b)  $\text{BI} + 0.85(\text{CH}_2>4) < 45$ ;

as measured over the hydrocarbon basestock as a whole. Preferably, the wax isomerate basestocks to be used in the lubricating oils of the present invention have a biodegradability value of at least 50% under the OECD 301B test. In addition, these basestock components have pour points of about  $-25^\circ\text{C}$  or lower.

The formulated lubricant oils comprising these same paraffinic basestock components are also characterized by unexpectedly good low-temperature and high-temperature viscosities, with CCS viscosity at  $-15^\circ\text{C}$  of not more than about 3500 cP, and with a kinematic viscosity at  $100^\circ\text{C}$  of about 5 cSt or greater. Desirable multigraded oils obtained using these basestocks may include 0W-, 5W-, 10W-, and 15W-XX grades ( $\text{XX} = 20-60$ ), and more specifically, for example, SAE 0W-30, 0W-40, and 15W-50.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 compares the low-temperature CCS viscometric properties of the primary liquid hydrocarbon basestocks (e.g., FTWI, or Fischer-Tropsch Wax Isomerate) of the present invention with typical hydroprocessed lubricant basestocks.

Figure 2 illustrates the parameters of BI (branching index) and  $\text{CH}_2>4$  (branching proximity, defined as a percentage), as set forth in formulas (a) and (b), of the wax-isomerate basestock compositions disclosed herein.

Figure 3 is a comparison of dynamic viscosities (DV @ -40°C), as measured by CCS method ASTM D5392, and kinematic viscosities (KV @ 100°C) of various hydrocarbon fluids, including, e.g., conventional hydro-cracked stocks, indicated as HDC, and FTWI basestocks of the present invention. The solid line represents the viscosity trend of the FTWI basestocks of this invention. The dotted line (parallel to the FTWI trend line) represents a boundary between the dynamic viscosity of the HDC oils and that of the FTWI oils.

Figure 4 illustrates the low-temperature viscosity (MRV and CCS) plus viscosity index (VI) for a typical series of basestocks utilized in the present invention. In this illustration, the basestocks are matched in viscosity at 6 cSt at 100°C, but differ from one another in pour point.

#### DETAILED DESCRIPTION OF THE INVENTION

The particular wax isomerate basestocks described herein broadly encompass basestocks which may be used in lubricant formulations. Surprisingly, the compositions of the wax isomerate basestocks as described herein generally do not predict the suitability of these same basestocks as lubricant components in the formulated lubricants of this invention. Rather, additional performance limits (*e.g.* basestock performance properties such as pour point, MRV viscosity, MRV yield stress, and viscosity index) must also be considered in identifying suitable wax isomerate basestocks which could be used in the lubricant formulations described herein.

Additionally, the suitability of the wax isomerate basestocks defined herein may be further limited by the interaction of such basestocks with other lubricant components (*e.g.* one or more additives, and optionally other base-

stocks) and may further be limited by performance of the finished fully formulated lubricant composition. Such performance limitations may include, for example, one or more of the following: CCS viscosity, MRV viscosity, MRV yield stress.

The formulated lubricating oils of the present invention comprise one or more wax isomerate basestocks in combination with other lubricating components. Such formulated oils include numerous functional fluids, including without limitation, engine oils, gear oils, transmission oils, and industrial oils. The present invention will be described with primary reference to engine oils, which represent the prime utility of the invention, but it is also applicable to other classes of oils as noted above.

The formulated lubricants of the present invention are capable of meeting a low-temperature grade of "0W," implying a cold cranking viscosity (ASTM D 5293) of not more than 3250 cP maximum at -30°C. These 0W oils necessarily have a very low viscosity at low temperatures in order to meet the extreme low-temperature fluidity requirement. Since the low viscosity base oils required to meet this portion of the specification have a low viscosity at the 100°C temperature used for establishing the high-temperature viscosity grade, as well as at actual engine operating temperatures, the 0W cross-graded oil is very difficult to achieve. However, by combining the present components, it has been found possible to produce oils conforming to the 0W requirement. Thus, the excellent low temperature oils of the present invention are 0W grade oils such as 0W-20, 0W-30, and 0W-40.

The advantages of the present invention may also be secured in other oils with a significant low-temperature performance requirement, for example, 5W and 10W oils with a high-temperature grade of 20 or 30 or higher. The utility of

the wax isomerates described herein increases as the range of the crossgrade (i.e., difference between low-temperature and high-temperature requirements) gets wider.

Although indicated by a low-temperature performance rating, e.g., 0W or W, the present oils are highly satisfactory under high-temperature operating conditions. In commercial use, the viscosities characteristic of these low-temperature ratings translate into improved fuel economy in actual operation. Thus, in addition to providing ready starting and improved lubrication from start-up, the present oils result in better fuel mileage and overall economy.

#### THE PRIMARY BASESTOCK COMPONENT

The primary basestocks of the present invention comprise paraffinic hydrocarbon components in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ( $\text{CH}_2>4$ ), are such that:

- (a)  $\text{BI} - 0.5(\text{CH}_2>4) > 15$ ; and
- (b)  $\text{BI} + 0.85(\text{CH}_2>4) < 45$ ;

as measured over the hydrocarbon basestock as a whole.

The hydrocarbon fluids of the present invention may have BI greater than 25.4, and Branching Proximity ( $\text{CH}_2>4$ ) less than 22.5, but more preferably have BI greater than 26.1 and Branching Proximity ( $\text{CH}_2>4$ ) less than 22.2, although any composition meeting the limitations of formula (a) and (b) is intended to be within the scope of the present invention. Measurement of the branching characteristics of the liquid hydrocarbons according to the present invention was

halo, amino,  $C_{1-5}$  alkyloxy and nitro; where  $R^1$  and  $R^3$  are selected from  $C_{1-5}$  alkylene, 5 or 6 membered cycloalkylene or heterocyclyl,  $-(CH_2CH_2-O)_p-$ ,  $-(CH_2CH_2CH_2-O)_p-$ ,  $R^2$  is selected from  $-O-$ ,  $-S-$ ,  $-S-S-$ ,  $-NR-$ ,  $-NRC(O)O-$ ,  $-NRC(O)NR-$ , alkylenedioxy, and  $-C(O)-$ ,  $p$  is 1 to 8 and  $m$ ,  $n$  and  $R$  are as defined above.

More preferably the linking group is selected from  $C_{1-5}$  alkylene,  $C_{1-5}$  alkenylene,  $-(CH_2CH_2-O)_p-$ ,  $C_{1-5}$  alkanedioyl,  $C_{1-5}$  alkylenedicarbonyl,  $-(C_{1-5} alkylene)_m-R^2-(C_{1-5} alkylene)_n-$ ,  $-(CH_2CH_2O)_m-R^2-(CH_2CH_2O)_n-$ , optionally substituted with one or more substituents selected from  $C_{1-3}$  alkyl, hydroxy, halo,  $C_{1-3}$  alkyloxy; where  $R^2$  is selected from  $-O-$ ,  $-S-S-$ ,  $-NR-$  and  $NRC(O)NR-$ , where  $R$  is  $H$  or  $CH_3$ ,  $p$  is 1 to 4 and  $m$  and  $n$  are as defined above.

Most preferably the linking group  $Y$  is selected from  $-CH_2-$ ,  $-CH_2-CH_2-$ ,  $-CH_2-O-CH_2-$ ,  $-CHOHCHOH-$ ,  $-CH_2-S-S-CH_2-$  and  $-(CH_2)_2NHC(O)NH(CH_2)_2-$ .

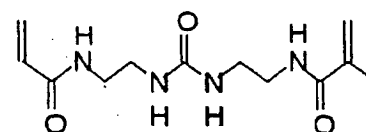
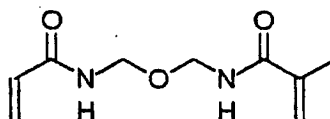
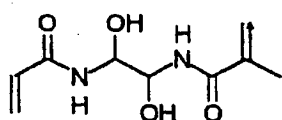
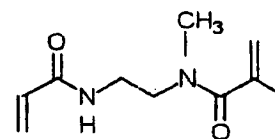
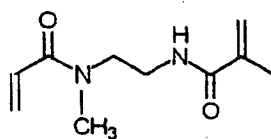
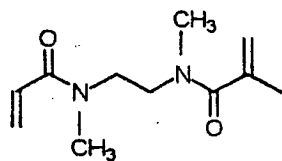
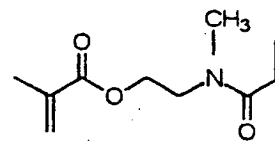
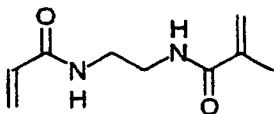
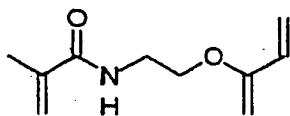
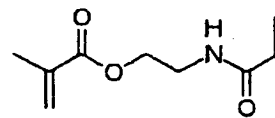
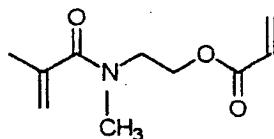
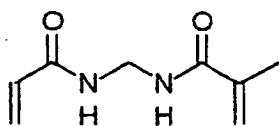
The crosslinking agents according to the present invention may be prepared by conventional methods. In one such method an appropriate substrate, i.e. a diamine, dialcohol, dithiol, aminoalcohol, thiolalcohol or thiolamine, is reacted with an equimolar amount of a reactive acryloyl or methacryloyl species, such as acryloyl chloride or methacryloyl chloride, in a suitable solvent such as chloroform or tetrahydrofuran, to form a monoacryloyl (or monomethacryloyl) intermediate. This intermediate may be isolated and purified before further reaction with an equivalent amount of the other reactive acryloyl or methacryloyl species, or the complete reaction may be carried out in two steps in a single pot. Reaction with the acryloyl species may be followed by reaction with the methacryloyl species or vice versa.

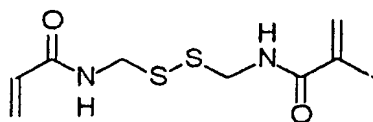
Where there is little or no reactivity differential between the reactive ends of the substrate, eg. for diamines, dialcohols and dithiols, it may be desirable to first protect one end of the substrate with an appropriate protecting group such as  $t$ -BOC. The other end can then be reacted with the reactive acryloyl or methacryloyl species to form a monoacryloyl (or

monomethacryloyl) intermediate. Removal of the protecting group is then followed by reaction with the other reactive methacryloyl or acryloyl species. It is also possible to achieve reaction predominantly at one end of such a substrate by controlling the pH of the reaction mixture.

- 5        Some of the monoacryloyl and monomethacryloyl intermediates are novel compounds and represent a further aspect of the invention.

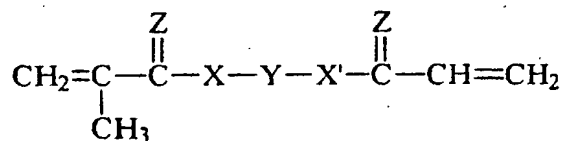
Preferred crosslinking agents useful in the present invention include the following:





While not wishing to be limited by theory it is believed that the more reactive vinyl group will be preferentially incorporated into the polymer chain, for example the methacryloyl end of the crosslinking agent reacts first with the monomer to yield a polymer with pendant acryloyl units. In this way long linear chains of the monomer incorporating primarily methacryloyl groups of the crosslinking agent would be produced first, before crosslinking of the linear polymeric chains starts to occur. It is believed that this delayed crosslinking produces a gel having a microporous structure more suitable for the separation of biomolecules than known gels prepared from symmetrical crosslinking agents such as BIS.

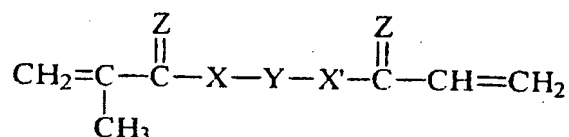
Some of the bisamide, bithioester and amidethioester crosslinking agents according to the present invention are novel and accordingly in another aspect the invention there is provided a compound of formula:



wherein X and X' are selected from -S- and -NR-, where R is H, alkyl or cycloalkyl, and

Y and Z are as defined above, provided that when X and X' are both -NR-, Y is not -CH<sub>2</sub>- and does not include a quaternary ammonium group.

Some of the amide-ester and thioester ester crosslinking agents of the present invention are also novel and, accordingly, in another aspect of the invention there is provided a compound of formula:



where one of X and X' is -O- and the other is selected from -S- and -NR-, where R is H, alkyl or cycloalkyl, and

Y and Z are as defined above; provided that Y is not C<sub>1-5</sub> alkylene and does not include a quarternary ammonium group, and that when the other of X and X' is -NH-, Y is not methyleneoxy-2-hydroxypropylene.

In addition to being useful crosslinking agents in the preparation of crosslinked polymer gel, the novel compounds, in view of their ability to form cross linked polymer networks, may be used as precursors for novel polymeric materials, or they may be used in admixtures with other polymerisable entities to produce novel crosslinked polymeric compounds to form products such as optical lenses, dental cements, surface coatings, plastic films, heat resistant plastics and adhesives. These compounds also have potential as biologically active compounds (e.g. antitumour agents).

The gels of the present invention may be prepared by conventional methods. They may be prepared in a variety of polymer concentrations, depending on the sizes of the molecules to be separated. Polyacrylamide gels crosslinked with BIS are commonly used to separate DNA fragments less than 1kb in length. For this purpose the gels are prepared having acrylamide concentrations in the range of about 3.5 to 20%. Gels having a concentration of 3.5% are useful for separating DNA fragments of about 100 to 1000 nucleotides while gels having an acrylamide concentration of about 20% are useful for separating fragments having from about 10 to 100 nucleotides.



Since the microporous structure of the gels according to the present invention is dependent on the particular crosslinking agent used, as well as the monomer concentration, the optimum monomer concentration for a particular biomolecule size range may differ somewhat from the optimum monomer concentrations known for acrylamide/BIS systems. The optimum concentration can be readily determined from standard trial runs.

Generally, however, the crosslinking agent can be employed in an amount of approximately 1 to 30 wt.%, preferably 2 to 10 wt.%, based on the total weight of the monomer and the crosslinking agent (%C). For the total gel concentration, monomers may be employed in approximately 1 to 50 wt%, preferably 1.5 to 20 wt%, based on total solution volume (%T).

The crosslinking polymerization reaction by which the novel gels of this invention are prepared is generally carried out in an aqueous medium and can be initiated by known initiators or polymerization catalysts.

Suitable free radical-providing initiator systems are benzoyl peroxide, t-butylhydroperoxide, lauroyl peroxide, cumene hydroperoxide, tetralin peroxide, acetyl peroxide, caproyl peroxide, t-butylperbenzoate, t-butylidiphenylphthalate, methylethylketone peroxide, hydrogen peroxide- $\text{Fe}^{2+}$ -ascorbic acid, riboflavin-light, methylene blue-light, and various persulfate salts in conjunction with N,N,N',N'-tetramethylethylenediamine (TEMED), diethylmethylenediamine (DEMED), 3-dimethylaminopropionitrile (DMAPN) or similar reagents and ammonium persulfate-metabisulfite.

Another class of free radical generating initiators are azocompounds such as azodiisobutyronitrile, azodiisobutyramide, azobis (dimethylvaleronitrile), azobis (methylbutyronitrile), dimethyl, diethyl, or dibutylazobismethylvalerate. These and similar reagents contain a N,N double bond attached to aliphatic carbon atoms, at least one of which is tertiary. The amount and type of initiator is generally indicated by the nature and concentrations of the monomer and crosslinking agent used. The optimum amount of initiator is also affected by the presence of any

Table 1

Buffer	pH
Citrate-phosphate	3.2
Succinate	5.2
Phosphate-magnesium sulfate	6.8
Tris-EDTA-acetate	7.2
Tris-HCl-magnesium sulfate	7.4
Tris-EDTA-acetate	7.8
Tris-magnesium chloride	8.0
Tris-EDTA-borate	8.3
Tris-EDTA-borate	8.6
Tris-EDTA-lactate	8.6
Tris-veronal	8.6
Veronal	9.2
Tris-EDTA-borate	9.5
Tris-EDTA-phosphate	8.6
Tris-glycine	8.8
Tris-glycine-SDS	8.8
Sodium phosphate	7.5
Sodium-phosphate SDS	7.5
Ethanolamine/GABA *	9.5-10
Tris/acetate/GABA	9.6-10.2
Ammediol/GABA	9.6-10.2
Ammediol/HCl	9.6-10.2
Tris-HCl	9.3-9.6

\* GABA = gamma, amino butyric acid

In addition to the analytical and preparative separation of biomolecules, the gels according to the present invention may be used to estimate molecular weights, and elucidate composition of complex mixtures. The gels may also be used in the sequencing of proteins and DNA, as polyelectrolytes, and may find use in environmental and quality control applications.

The performance of known gels has so far been limited by a number of factors including (a) restriction on pore size range available (thereby restricting the molecular weight range of fragments which can be separated), (b) the susceptibility of some gels to hydrolysis in slightly alkaline media, or to premature mechanical degradation and (c) high background staining caused by the amide linkages of BIS. An advantage of the present invention is the ability to control or modify gel formation to produce a gel having the desired characteristics (e.g. pore size, mechanical stability, alkaline stability, background staining etc.) by selecting an appropriate asymmetrical crosslinking agent.

In order to more clearly describe the invention reference will be made to the following examples and drawings which describe some preferred embodiments of the invention. However the particularity of the examples and drawings is not to be understood to supersede the generality of the preceding description.

### **BRIEF DESCRIPTION OF DRAWINGS**

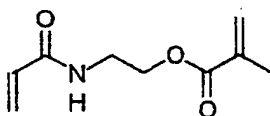
Referring to the drawings:

Figure 1 shows the separation of a standard protein mixture achieved using gels according to the present invention (Gels B, C and D) compared to a standard BIS gel (Gel A), where the concentrations of acrylamide and crosslinking agent are equivalent, on a mole:mole basis, with a 10%T 3%C BIS gel.

Figure 2 shows the separation of the same standard protein mixture of Figure 1 where the concentrations of acrylamide and crosslinking agent are equivalent, on a mole:mole basis, with a 15%T 3%C BIS gel.

### Examples:

#### Example 1: Preparation of 2-Methacrylethylacrylamide



Acryloyl chloride (25 mmol, 2.0 cm<sup>3</sup>) in chloroform (25 cm<sup>3</sup>) was added dropwise to a stirred solution of ethanolamine (50 mmol, 3.0 cm<sup>3</sup>) in chloroform (50 cm<sup>3</sup>) at 0°C. After the addition was complete, the reaction mixture was stirred at 0°C for a further 2h. The monohydrochloride precipitate was removed by filtration and the filtrate evaporated under reduced pressure to give the crude product as a yellow oil. This was then taken up in a slurry of basic alumina in chloroform, and stirred at room temperature for 18 h. Removal of the alumina and concentration of the solution then gave the desired (2-hydroxy)ethylacrylamide as a clear colorless oil. (2.5 g, 87%).  $\delta_H$  (400MHz; CDCl<sub>3</sub>) 7.06 (1H, br s), NH; 6.24 (1H, dd, J 17.0, 1.8 Hz), HC=CH<sub>a</sub>H<sub>b</sub>; 6.17 (1H, dd, J 17.0, 9.8 Hz), HC=CH<sub>a</sub>H<sub>b</sub>; 5.62 (1H, dd, J 9.9, 1.8 Hz), HC=CH<sub>a</sub>H<sub>b</sub>; 4.13 (1H, s), OH; 3.69 (2H, t, J 5.1 Hz), CH<sub>2</sub>OH; 3.43 (2H, td, J 5.6, 4.9 Hz), NHCH<sub>2</sub>.  $\delta_C$  (75.4 MHz; CDCl<sub>3</sub>) 166.76, C=O; 130.50, HC=CH<sub>2</sub>; 126.81, HC=CH<sub>2</sub>; 61.70, CH<sub>2</sub>OH; 42.41, NHCH<sub>2</sub>. Found: M<sup>+</sup> 115.14.

To a stirred solution of N-(2-hydroxyethyl)acrylamide (7.0 mmol, 0.8 g) and triethylamine (7.7 mmol, 1.1 cm<sup>3</sup>) in chloroform (30 cm<sup>3</sup>) at room temperature, was added dropwise, a solution of methacryloyl chloride (7.7 mmol, 0.8 cm<sup>3</sup>) in chloroform (15 cm<sup>3</sup>) under an atmosphere of nitrogen.

After the addition was complete, the reaction mixture was stirred for 16h.

The reaction mixture was then washed with 2M HCl, and the organic

fractions collected, dried and concentrated under reduced pressure to give

the crude product as a yellow oil. This was then taken up in a slurry of basic

5 alumina in chloroform and stirred at room temperature for 18 hr. Removal of

the alumina and concentration of the filtrate gave a yellow oil which was

subjected to flash chromatography (silica gel, diethyl ether : hexane :

methanol elution) to afford 2-methacrylethylacrylamide ( $R_f$  0.51) as a clear

yellow oil (0.77 g, 61%).  $\delta_{11}$  (400MHz;  $CDCl_3$ ) 6.20 (1H, br m),  $NH$ ; 6.26 (1H,

10 dd, J 17.0, 1.5 Hz),  $RHNOCC\dot{H}=CH_cH_d$ ; 6.11 (1H, dd, J 17.0, 10.3 Hz),

$RHNOCC\dot{H}=CH_cH_d$ ; 6.10 (1H, br s),  $ROO(H_3C)C=CH_aH_b$ ; 5.63 (1H, dd, J 10.3,

1.5 Hz),  $RHNOCC\dot{H}=CH_aH_b$ ; 5.58 (1H, m),  $ROO(H_3C)C=CH_aH_b$ ; 4.26 (2H, t, J

5.4 Hz),  $\dot{C}H_2OC=O$ ; 3.63 (2H, td, J 5.6, 5.4 Hz),  $\dot{C}H_2NHC=O$ ; 1.92 (3H, s)  $\dot{C}H_3$ .

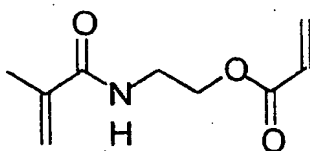
$\delta_C$  (75.4 MHz;  $CDCl_3$ ) 167.48,  $OC=O$ ; 165.69,  $HNC=O$ ; 135.86,

15  $ROO(H_3C)\dot{C}=CH_2$ ; 130.56,  $RHNOCC\dot{H}=CH_2$ ; 126.67,  $RHNOCC\dot{H}=\dot{C}H_2$ ;

126.13,  $ROO(H_3C)C=\dot{C}H_2$ ; 63.32,  $\dot{C}H_2OC=O$ ; 38.89,  $\dot{C}H_2NHC=O$ ; 18.23.  $\dot{C}H_3$ .

Found:  $M^+$  183.22.

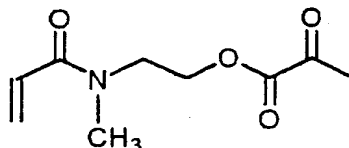
## Example 2: Preparation of 2-Acrylethylmethacrylamide



Methacryloyl chloride (25 mmol, 2.4 cm<sup>3</sup>) in chloroform (25 cm<sup>3</sup>) was added dropwise to a stirred solution of ethanolamine (50 mmol, 3.0 cm<sup>3</sup>) in chloroform (50 cm<sup>3</sup>) at 0/C. After the addition was complete, the reaction mixture was stirred at 0/C for a further 2h. The monohydrochloride precipitate was removed by filtration and the filtrate evaporated under reduced pressure to give the crude product as a yellow oil. This was then

taken up in a slurry of basic alumina in chloroform, and stirred at room temperature for 18 h. Removal of the alumina and concentration of the solution then gave the (2-hydroxy)-ethylmethacrylamide product as a clear colorless oil. (3.2g, 96%).  $\delta_{\text{H}}$  (400MHz;  $\text{CDCl}_3$ ) 6.57 (1H, br m),  $\text{NH}$ ; 6.27 (1H, dd, J 17.0, 1.5 Hz),  $\text{HC}=\text{CH}_a\text{H}_b$ ; 6.14 (1H, dd, J 17.0, 10.0 Hz),  $\text{HC}=\text{CH}_a\text{H}_b$ ; 5.65 (1H, dd, J 10.0, 1.5 Hz),  $\text{HC}=\text{CH}_a\text{H}_b$ ; 3.74 (2H, t, J 4.9 Hz),  $\text{CH}_2\text{OH}$ ; 3.48 (2H, td, J 5.6, 4.9 Hz),  $\text{NHCH}_2$ ; 3.37 (1H, s),  $\text{OH}$ .  $\delta_{\text{C}}$  (75.4 MHz;  $\text{CDCl}_3$ ) 166.76,  $\text{C}=\text{O}$ ; 130.50,  $\text{HC}=\text{CH}_2$ ; 126.81,  $\text{HC}=\text{CH}_2$ ; 61.70,  $\text{CH}_2\text{OH}$ ; 42.41,  $\text{NHCH}_2$ . Found:  $\text{M}^+$  129.17.

To a stirred solution of N-(2-hydroxyethyl)methacrylamide (10 mmol, 1.3 g) and triethylamine (11 mmol, 1.5  $\text{cm}^3$ ) in chloroform (40  $\text{cm}^3$ ), was added dropwise, a solution of acryloyl chloride (11 mmol, 0.9  $\text{cm}^3$ ) in chloroform (20  $\text{cm}^3$ ) at room temperature under a nitrogen atmosphere. After the addition was complete, the reaction mixture was stirred for a further 16 h. The usual work-up as for example 1 then gave the crosslinking monomer, 2-acrylethylmethacrylamide ( $R_f$  0.54) as a clear, colorless oil (0.6 g, 32%).  $\delta_{\text{H}}$  (400MHz;  $\text{CDCl}_3$ ) 6.45 (1H, br m),  $\text{NH}$ ; 6.38 (1H, dd, J 17.8, 2.0 Hz),  $\text{ROOCH}=\text{CH}_a\text{H}_b$ ; 6.08 (1H, dd, J 17.8, 8.9 Hz),  $\text{ROOCH}=\text{CH}_a\text{H}_b$ ; 5.82 (1H, dd, J 8.9, 2.0 Hz),  $\text{ROOCH}=\text{CH}_a\text{H}_b$ ; 5.66 (1H, s),  $\text{RHNOC}(\text{H}_3\text{C})\text{C}=\text{CH}_c\text{H}_d$ ; 5.29 (1H, s),  $\text{RHNOC}(\text{H}_3\text{C})\text{C}=\text{CH}_c\text{H}_d$ ; 4.25 (2H, t, J 4.9 Hz),  $\text{CH}_2\text{OCO}$ ; 3.57 (2H, td, J 4.9, 4.7 Hz),  $\text{CH}_2\text{NHCO}$ ; 1.94 (3H, s),  $\text{CH}_3$ .  $\delta_{\text{C}}$  (75.4 MHz;  $\text{CDCl}_3$ ) 168.52,  $\text{HNC}=\text{O}$ ; 166.22,  $\text{OC}=\text{O}$ ; 139.60,  $\text{RHNOC}(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 131.34,  $\text{ROOCH}=\text{CH}_2$ ; 127.83,  $\text{ROOCH}=\text{CH}_2$ ; 119.69,  $\text{RHNOC}(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 63.07,  $\text{CH}_2\text{OC}=\text{O}$ ; 38.97,  $\text{CH}_2\text{NHC}=\text{O}$ ; 18.43,  $\text{CH}_3$ . Found:  $\text{M}^+$  183.22.

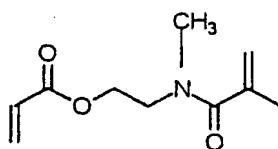
**Example 3: Preparation of N-Methyl, N-acryloyl-2-ethylmethacrylate**

Acryloyl chloride (25 mmol, 2.0 cm<sup>3</sup>) in chloroform (25 cm<sup>3</sup>) was added dropwise to a stirred solution of 2-(methylamino)ethanol (50 mmol, 4.0 cm<sup>3</sup>) in chloroform (50 cm<sup>3</sup>) at 0°C. After the addition was complete, the reaction mixture was stirred at 0°C for a further 2h. The monohydrochloride precipitate was removed by filtration and the filtrate evaporated under reduced pressure to give the crude product as a yellow oil. This was then taken up in a slurry of basic alumina in chloroform, and stirred at room temperature for 18 h. Removal of the alumina and concentration of the solution then gave the desired N-methyl, N-acryloyl-2-ethanol as a clear colorless oil (2.77g, 86%).  $\delta_H$  (300MHz; CDCl<sub>3</sub>) 6.47 (1H, dd, J 17.0, 1.8 Hz), HC=CH<sub>a</sub>H<sub>b</sub>; 6.23 (1H, dd, J 17.0, 9.9 Hz), HC=CH<sub>a</sub>H<sub>b</sub>; 5.57 (1H, dd, J 10.0, 1.9 Hz), HC=CH<sub>a</sub>H<sub>b</sub>; 4.07 (1H, s), OH; 3.77 (2H, t, J 5.1 Hz), CH<sub>2</sub>OH; 3.46 (2H, td, J 5.6, 4.9 Hz), NCH<sub>2</sub>; 3.10 (3H, br m), N(CH<sub>3</sub>).  $\delta_C$  (75.4 MHz; CDCl<sub>3</sub>) 166.85, C=O; 130.53, HC=CH<sub>2</sub>; 126.85, HC=CH<sub>2</sub>; 60.88, CH<sub>2</sub>OH; 43.76, NCH<sub>2</sub>. Found: M<sup>+</sup> 129.17.

To a stirred solution of intermediate (7.0 mmol, 0.8 g) and triethylamine (7.7 mmol, 1.1 cm<sup>3</sup>) in chloroform (30 cm<sup>3</sup>) at room temperature, was added dropwise, a solution of methacryloyl chloride (7.7 mmol, 0.8 cm<sup>3</sup>) in chloroform (15 cm<sup>3</sup>) under an atmosphere of nitrogen. The work-up as for example 1 then afforded N-methyl, N-acryloyl-2-ethylmethacrylate as a clear yellow oil (0.65g, 47%).  $\delta_H$  (400MHz; CDCl<sub>3</sub>) 6.54 (1H, dd, J 17.8, 10.3 Hz), N(CH<sub>3</sub>)CH=CH<sub>a</sub>H<sub>b</sub>; 6.33 (1H, dd, J 17.8, 2.0 Hz), N(CH<sub>3</sub>)CH=CH<sub>a</sub>H<sub>b</sub>; 6.15 (1H, br m), O<sub>2</sub>C(H<sub>3</sub>C)C=CH<sub>c</sub>H<sub>d</sub>; 5.90 (1H, br m), O<sub>2</sub>C(H<sub>3</sub>C)C=CH<sub>c</sub>H<sub>d</sub>; 5.63 (1H, dd, J 10.1, 2.0 Hz), N(CH<sub>3</sub>)CH=CH<sub>a</sub>H<sub>b</sub>; 4.09 (2H,

t, J 4.9 Hz),  $\text{CH}_2\text{OCO}$ ; 3.48 (2H, td, J 4.9, 4.7 Hz),  $\text{CH}_2\text{N}(\text{CH}_3)\text{CO}$ ; 3.03 (3H, s),  $\text{N}(\text{CH}_3)$ ; 1.88 (3H, s),  $\text{CH}_3$ .  $\delta_{\text{C}}$  (75.4 MHz;  $\text{CDCl}_3$ ) 167.50,  $\text{OC}=\text{O}$ ; 166.85,  $\text{N}(\text{CH}_3)\text{C}=\text{O}$ ; 136.46,  $\text{RO}_2\text{C}(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 130.92,  $\text{RN}(\text{CH}_3)\text{OCH}=\text{CH}_2$ ; 126.79,  $\text{RN}(\text{CH}_3)\text{OCH}=\text{CH}_2$ ; 124.10,  $\text{RO}_2\text{C}(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 61.75,  $\text{CH}_2\text{OC}=\text{O}$ ; 45.33,  $\text{CH}_2\text{N}(\text{CH}_3)\text{C}=\text{O}$ ; 35.61,  $\text{N}(\text{CH}_3)$ ; 17.20,  $\text{CH}_3$ . Found:  $\text{M}^+$  197.25.

#### Example 4: Preparation of N-Methyl, N-methacryloyl-2-ethylacrylate



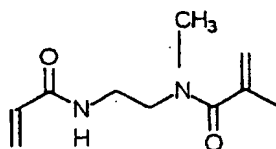
Methacryloyl chloride (25 mmol, 2.4 cm<sup>3</sup>) in chloroform (25 cm<sup>3</sup>) was added dropwise to a stirred solution of 2-(methylamino)ethanol (50 mmol, 4.0 cm<sup>3</sup>) in chloroform (50 cm<sup>3</sup>) at 0°C. After the addition was complete, the reaction mixture was stirred at 0°C for a further 2h. The monohydrochloride precipitate was removed by filtration and the filtrate evaporated under reduced pressure to give the crude product as a yellow oil. This was then taken up in a slurry of basic alumina in chloroform, and stirred at room temperature for 18 h. Removal of the alumina and concentration of the solution then gave the desired N-methyl, N-methacryloyl-2-ethanol intermediate as a clear colorless oil (3.22g, 90%).  $\delta_{\text{H}}$  (300MHz;  $\text{CDCl}_3$ ) 5.76 (1H, br m),  $\text{N}(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 5.45 (1H, br m),  $\text{N}(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 4.15 (1H, s),  $\text{OH}$ ; 3.82 (2H, t, J 5.1 Hz),  $\text{CH}_2\text{OH}$ ; 3.53 (2H, td, J 5.6, 4.9 Hz),  $\text{NCH}_2$ ; 3.14 (3H, br m),  $\text{N}(\text{CH}_3)$ ; 1.97 (3H, s),  $\text{CH}_3$ .  $\delta_{\text{C}}$  (75.4 MHz;  $\text{CDCl}_3$ ) 171.88,  $\text{C}=\text{O}$ ; 141.05,  $(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 126.81,  $(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 62.35,  $\text{CH}_2\text{OH}$ ; 43.21,  $\text{NCH}_2$ ; 36.56,  $\text{N}(\text{CH}_3)$ ; 19.53,  $\text{CH}_3$ . Found:  $\text{M}^+$  143.20.

To a stirred solution of intermediate (7.0 mmol, 0.8 g) and triethylamine (7.7 mmol, 1.1 cm<sup>3</sup>) in chloroform (30 cm<sup>3</sup>) at room temperature, was added dropwise, a solution of acryloyl chloride (7.7 mmol,



0.6 cm<sup>3</sup>) in chloroform (15 cm<sup>3</sup>) under an atmosphere of nitrogen. The work-up as for example 1 then yielded N-methyl, N-acryloyl-2-ethylmethacrylate as a clear yellow oil (0.72g, 52%).  $\delta_{11}$  (400MHz; CDCl<sub>3</sub>) 6.38 (1H, dd, J 17.0, 1.5 Hz), O<sub>2</sub>CCH=CH<sub>c</sub>H<sub>d</sub>; 6.11 (1H, dd, J 17.0, 10.3 Hz), O<sub>2</sub>CCH=CH<sub>c</sub>H<sub>d</sub>; 5.77 (1H, dd, J 10.3, 1.5 Hz), O<sub>2</sub>CCH=CH<sub>c</sub>H<sub>d</sub>; 5.72 (1H, br m), N(H<sub>3</sub>C)C=CH<sub>a</sub>H<sub>b</sub>; 5.38 (1H, br m), N(H<sub>3</sub>C)C=CH<sub>a</sub>H<sub>b</sub>; 4.10 (2H, t, J 5.4 Hz), CH<sub>2</sub>OC=O; 3.47 (2H, td, J 5.6, 5.4 Hz), CH<sub>2</sub>N(CH<sub>3</sub>)C=O; 3.04 (3H, s), N(CH<sub>3</sub>); 1.95, (3H, s) CH<sub>3</sub>.  $\delta_C$  (75.4 MHz; CDCl<sub>3</sub>) 172.80, N(H<sub>3</sub>C)C=O; 166.70, OC=O; 140.16, N(H<sub>3</sub>C)C=CH<sub>2</sub>; 131.85, RO<sub>2</sub>CCH=CH<sub>2</sub>; 128.80, RO<sub>2</sub>CCH=CH<sub>2</sub>; 126.67, N(H<sub>3</sub>C)CH=CH<sub>2</sub>; 1119.56, N(H<sub>3</sub>C)C=CH<sub>2</sub>; 61.60, CH<sub>2</sub>OC=O; 45.47, CH<sub>2</sub>N(CH<sub>3</sub>)C=O; 36.35, N(CH<sub>3</sub>); 19.24, CH<sub>3</sub>. Found: M<sup>+</sup> 197.25.

**Example 5: Preparation of N-Methyl, N-methacryloyl, N'-acryloyl-ethylenediamine**



To a stirred solution of N-methyl-ethylenediamine (0.10 mol, 8.8 cm<sup>3</sup>) in dioxane (50 cm<sup>3</sup>), at room temperature and under a nitrogen atmosphere, was added a solution of S-tert-butyloxycarbonyl-4,6-dimethyl-2-mercaptopyrimidine (0.05 mol, 12 g) in dioxane (50 cm<sup>3</sup>), dropwise, over 3 h. After the addition was complete, the solution was stirred at room temperature for a further 15 h. The precipitate which formed (4, 6-dimethyl-2-mercaptopyrimidine) was removed from the solution, and the filtrate conc. *in vacuo* to half its original volume (50 cm<sup>3</sup>). To this residue, was added water (80 cm<sup>3</sup>) and the solution then left to stand at room temperature for 15 min. The bis-(t-BOC)-diamine precipitate was then removed, and the filtrate conc. *in vacuo*. To the residue was added water (80 cm<sup>3</sup>), and the solution subsequently saturated with sodium chloride. This saturated solution was

extracted with ethyl acetate (4x40 cm<sup>3</sup>), and the organic extracts combined. dried (MgSO<sub>4</sub>), filtered, and conc. *in vacuo* to give an oil. This oil was dissolved in water (50 cm<sup>3</sup>) and acidified to pH 3 with 1M hydrochloric acid. The solution was then extracted with ethyl acetate (3x100 cm<sup>3</sup>). The aqueous layer was then collected, decolourized with activated charcoal and filtered over Celite. The filtrate was then conc. *in vacuo*. If necessary, fractional recrystallization from room temperature methanol was used to separate the required product from any diamine dihydrochloride by-product. The filtrate was then conc. *in vacuo*. The product was isolated by trituration from hexane, to give a fine off-white solid which consisted of a mixture of N-t-BOC, N-methyl-ethylenediamine monohydrochloride and N-t-BOC, N'-methyl ethylenediamine monohydrochloride in a 4 : 1 ratio (4.8 g, 45%). m.p. 104-105°C.  $\delta_H$  (400MHz; methanol-d<sub>4</sub>) 3.52-3.37 (2H, t, J 4.8Hz),  $\underline{CH_2NH}$ ; 3.31 (2H, t, J 4.8Hz),  $\underline{CH_2NH(CH_3)}$ ; 2.81 (3H, s),  $NCH_3$ ; 1.43 (9H, s),  $C(\underline{CH_3})_3$ .  $\delta_C$  (75.4MHz; methanol-d<sub>4</sub>) 157.88,  $\underline{C=O}$ ; 81.60  $\underline{C(CH_3)_3}$ ; 47.47,  $\underline{CH_2NH(CH_3)}$ ; 39.09,  $\underline{CH_2NH}$ ; 28.65,  $C(\underline{CH_3})_3$ . Found:  $M^+$  210.72.

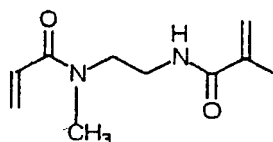
The intermediate N-t-BOC, N-methyl-ethylenediamine monohydrochloride (10.0 mmol, 2.11 g) was stirred with 2M NaOH (11 cm<sup>3</sup>) at room temperature for 10 min. The solution was then cooled to 0°C, and to this, was added a solution of acryloyl chloride (11.0 mmol, 0.9 cm<sup>3</sup>) in chloroform (30 cm<sup>3</sup>), dropwise. After the addition was complete, the reaction mixture was stirred at 0°C for a further 1 h. The organic and aqueous phases were then separated, and the aqueous phase extracted with chloroform. The organic extracts were combined, dried (MgSO<sub>4</sub>), filtered and conc. *in vacuo*, to give the crude product. The crude product was stirred at room temperature over a slurry of basic alumina in chloroform for 18 hr. Removal of the alumina and concentration of the filtrate then gave a pale yellow oil. Purification by flash chromatography (silica gel, diethyl ether : hexane : methanol elution) afforded the major isomer N-t-BOC, N-methyl, N'-acryloyl-ethylenediamine ( $R_f$  0.27) as a pale yellow oil which solidified upon

standing. Trituration from hexane then gave the product as a white solid (1.55 g, 68%). m.p. 56 - 57/C.  $\delta_{\text{H}}$  (400MHz;  $\text{CDCl}_3$ ) 6.72 (1H, br s),  $\text{NH}$ ; 6.20 (1H, d, J 17.3 Hz),  $\text{CH}=\text{CH}_a\text{H}_b$ ; 6.05 (1H, dd, J 17.1, 10.3 Hz),  $\text{CH}=\text{CH}_a\text{H}_b$ ; 5.58 (1H, d, J 10.0 Hz),  $\text{CH}=\text{CH}_a\text{H}_b$ ; 3.43 (4H, m), 2 x  $\text{CH}_2$ ; 2.86 (3H, s),  $\text{N}(\text{CH}_3)$ ; 1.42 (9H, s),  $\text{C}(\text{CH}_3)_3$ .  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ , 50/C) 165.90,  $\text{NHOCCH}=\text{CH}_2$ ; 156.88,  $\text{NCO}_2\text{C}(\text{CH}_3)_3$ ; 131.11,  $\text{CH}=\text{CH}_2$ ; 125.56,  $\text{CH}=\text{CH}_2$ ; 79.87  $\text{C}(\text{CH}_3)_3$ ; 47.62,  $\text{CH}_2\text{NHCO}_2\text{C}(\text{CH}_3)_3$ ; 38.57,  $\text{CH}_2\text{N}(\text{CH}_3)\text{OCCH}=\text{CH}_2$ ; 34.62,  $\text{N}(\text{CH}_3)$ ; 28.31,  $\text{C}(\text{CH}_3)_3$ . Found:  $\text{M}^+$  228.31.

N-t-BOC, N-methyl, N'-acryloyl-ethylenediamine (2.5 mmol, 0.57 g) was stirred in a solution of 3M HCl in ethyl acetate (2.5  $\text{cm}^3$ ) at room temperature for 30 min. The solution was then conc. in vacuo to give the intermediate N-methyl, N'-acryloyl-ethylenediamine monohydrochloride as a clear yellow oil. This intermediate (2.5 mmol) was then stirred at room temperature in 2M NaOH (3  $\text{cm}^3$ ) for 10 min. This reaction mixture was cooled to 0°C, and to this, was added a solution of methacryloyl chloride (2.8 mmol, 0.27  $\text{cm}^3$ ) in chloroform (7  $\text{cm}^3$ ), dropwise, over 30 min. After the addition was complete, the reaction mixture was stirred at 0°C for a further 1 h. The organic and aqueous phases were then separated, and the aqueous phase extracted with chloroform. The organic extracts were combined, dried ( $\text{MgSO}_4$ ), filtered and conc. in vacuo, to give the crude product. The crude product was stirred at room temperature over a slurry of basic alumina in chloroform for 18 hr. Removal of the alumina and concentration of the filtrate then gave a pale yellow oil. Purification by flash chromatography (silica gel, diethyl ether : hexane : methanol elution) afforded N-methyl, N-methacryloyl, N'-acryloyl-ethylenediamine as a pale yellow oil (0.24g, 48%).  $\delta_{\text{H}}$  (300MHz;  $\text{CDCl}_3$ ) 6.79 (1H, br s),  $\text{NH}$ ; 6.2 (1H, d, J 17.1 Hz),  $\text{HC}=\text{CH}_a\text{H}_b$ ; 6.08 (1H, dd, J 17.1, 10.0),  $\text{HC}=\text{CH}_a\text{H}_b$ ; 5.59 (1H, d, J 10.0 Hz),  $\text{HC}=\text{CH}_a\text{H}_b$ ; 5.18 (br m),  $(\text{H}_3\text{C})\text{C}=\text{CH}_c\text{H}_d$ ; 5.00 (br m),  $(\text{H}_3\text{C})\text{C}=\text{CH}_c\text{H}_d$ ; 3.58 (4H, br m), 2 x  $\text{CH}_2$ ; 3.05, (3H, br m)  $\text{N}(\text{CH}_3)$ ; 1.90 (3H, br m),  $\text{CH}_3$ .  $\delta_{\text{C}}$  (75.4MHz;  $\text{CDCl}_3$ ) 170.92,  $\text{NOC}(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 162.87,  $\text{NHOCCH}=\text{CH}_2$ ; 139.39,  $(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ;

132.00,  $\text{HC}=\underline{\text{CH}}_2$ ; 125.42,  $\text{HC}=\underline{\text{CH}}_2$ ; 119.56,  $(\text{H}_3\text{C})\text{C}=\underline{\text{CH}}_2$ ; 44.97,  $\underline{\text{CH}}_2\text{CH}_2$ ;  
36.21,  $\text{CH}_2\underline{\text{CH}}_2$ ; 33.98,  $\text{N}(\underline{\text{CH}}_3)$ ; 19.24,  $\underline{\text{CH}}_3$ . Found:  $\text{M}^+$  196.26

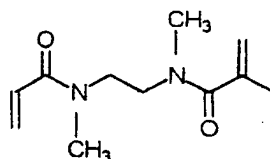
**Example 6: Preparation of N-Methyl, N-acryloyl, N'-methacryloyl-ethylenediamine**



The intermediate N-t-BOC, N-methyl-ethylenediamine monohydrochloride prepared in example 5 (10 mmol, 2.1 g) was stirred with 2M NaOH (11 cm<sup>3</sup>) at room temperature for 10 min. The solution was then cooled to 0°C, and to this, was added a solution of methacryloyl chloride (11 mmol, 1.1 cm<sup>3</sup>) in chloroform (30 cm<sup>3</sup>), dropwise. After the addition was complete, the reaction mixture was stirred at 0°C for a further 1 h. The organic and aqueous phases were then separated, and the aqueous phase extracted with chloroform. The organic extracts were combined, dried (MgSO<sub>4</sub>), filtered and conc. in vacuo, to give the crude product. The crude product was stirred at room temperature over a slurry of basic alumina in chloroform for 18 hr. Removal of the alumina and concentration of the filtrate then gave a pale yellow oil. Purification by flash chromatography (silica gel, diethyl ether : hexane : methanol elution) afforded N-t-BOC, N-methyl, N'-methacryloyl-ethylenediamine ( $R_f$  0.51) as a yellow oil (1.63 g, 67%).  $\delta_{\text{H}}$  (400MHz; CDCl<sub>3</sub>) 6.94 (1H, br s),  $\text{HNOC}(\text{H}_3\text{C})\text{C}=\underline{\text{CH}}_2\text{H}_b$ ; 5.74 (1H, br m),  $(\text{H}_3\text{C})\text{C}=\underline{\text{CH}}_2\text{H}_b$ ; 5.30 (1H, br m),  $(\text{H}_3\text{C})\text{C}=\underline{\text{CH}}_2\text{H}_b$ ; 3.43 (4H, br m), 2 x  $\underline{\text{CH}}_2$ ; 2.87 (3H, s),  $\text{N}(\underline{\text{CH}}_3)$ ; 1.93 (3H, br m),  $\underline{\text{CH}}_3$ ; 1.44 (9H, s),  $\text{C}(\underline{\text{CH}}_3)_3$ .  $\delta_{\text{C}}$  (75.4MHz; CDCl<sub>3</sub>) 168.52,  $\text{NHOC}(\text{H}_3\text{C})\text{C}=\underline{\text{CH}}_2$ ; 157.33,  $\text{NHCO}_2\text{C}(\text{CH}_3)_3$ ; 139.36,  $(\text{H}_3\text{C})\underline{\text{C}}=\underline{\text{CH}}_2$ ; 119.81,  $(\text{H}_3\text{C})\text{C}=\underline{\text{CH}}_2$ ; 80.85  $\underline{\text{C}}(\text{CH}_3)_3$ ; 47.32,  $\underline{\text{CH}}_2\text{N}(\text{CH}_3)\text{OC}(\text{H}_3\text{C})\text{C}=\underline{\text{CH}}_2$ ; 39.32,  $\underline{\text{CH}}_2\text{NHCO}_2\text{C}(\text{CH}_3)_3$ ; 34.68,  $\text{N}(\underline{\text{CH}}_3)$ ; 28.33,  $\text{C}(\underline{\text{CH}}_3)_3$ ; 18.47,  $\underline{\text{CH}}_3$ . Found:  $(\text{MH}^+)$  243.17178.

N-t-BOC, N'-methyl, N'-methacryloyl-ethylenediamine (2.5 mmol, 0.61 g) was stirred in a solution of 3M HCl in ethyl acetate (2.5 cm<sup>3</sup>) at room temperature for 30 min. The solution was then conc. *in vacuo* to give the intermediate N-methyl, N'-methacryloyl-ethylenediamine monohydrochloride as a clear yellow oil. This intermediate (2.5 mmol) was then stirred at room temperature in 2M NaOH (3 cm<sup>3</sup>) for 10 min. The reaction mixture was cooled to 0°C, and to this, was then added a solution of acryloyl chloride (2.8 mmol, 0.23 cm<sup>3</sup>) in chloroform (7 cm<sup>3</sup>), dropwise, over 30 min. After the addition was complete, the reaction mixture was stirred at 0°C for a further 1h. The organic and aqueous phases were then separated, and the aqueous phase extracted with chloroform. The organic extracts were combined, dried (MgSO<sub>4</sub>), filtered and conc. *in vacuo*, to give the crude product. The crude product was stirred at room temperature over a slurry of basic alumina in chloroform for 18 hr. Removal of the alumina and concentration of the filtrate then gave a pale yellow oil. Purification by flash chromatography (silica gel, diethyl ether : hexane : methanol elution) then gave the crosslinker N-methyl, N-acryloyl, N'-methacryloyl-ethylenediamine as a pale yellow oil (0.26g, 53%).  $\delta_H$  (300MHz; CDCl<sub>3</sub>) 7.01 (1H, br s), NH; 6.50 (1H, dd, J 16.8, 10.4 Hz), HC=CH<sub>a</sub>H<sub>b</sub>; 6.22 (1H, dd, J 12.4, 2.0), HC=CH<sub>a</sub>H<sub>b</sub>; 5.66 (br m), (H<sub>3</sub>C)C=CH<sub>c</sub>H<sub>d</sub>; 5.61 (1H, d, J 10.5 Hz), HC=CH<sub>a</sub>H<sub>b</sub>; 5.23 (br m), (H<sub>3</sub>C)C=CH<sub>c</sub>H<sub>d</sub>; 3.57 (2H, br m), CH<sub>2</sub>; 3.43 (2H, br m), CH<sub>2</sub>; 3.00, (3H, br m) N(CH<sub>3</sub>); 1.85 (3H, br m), CH<sub>3</sub>.  $\delta_C$  (75.4MHz; CDCl<sub>3</sub>, 50°C) 166.10, NHOC(H<sub>3</sub>C)C=CH<sub>2</sub>; 165.04, NOCHC=CH<sub>2</sub>; 140.40, (H<sub>3</sub>C)C=CH<sub>2</sub>; 130.92, HC=CH<sub>2</sub>; 126.01, HC=CH<sub>2</sub>; 118.50, (H<sub>3</sub>C)C=CH<sub>2</sub>; 44.83, CH<sub>2</sub>CH<sub>2</sub>; 35.47, CH<sub>2</sub>CH<sub>2</sub>; 34.12, N(CH<sub>3</sub>); 18.50, CH<sub>3</sub>. Found: M<sup>+</sup> 196.26.

**Example 7: Preparation of N-Acryloyl, N'methacryloyl, N, N'dimethyl-ethylenediamine**



**Method (a)**

To a stirred solution of N, N'-dimethyl-ethylenediamine (0.10 mol, 12.4 cm<sup>3</sup>) in dioxane (50 cm<sup>3</sup>), at room temperature and under a nitrogen atmosphere, was added a solution of S-tert-butyloxycarbonyl-4,6-dimethyl-2-mercaptopyrimidine (0.05 mol, 12 g) in dioxane (50 cm<sup>3</sup>), dropwise, over 3 h. After the addition was complete, the solution was stirred at room temperature for a further 15 h. The work-up as in example 5 gave the product which was isolated by trituration from hexane, to give N-t-BOC, N, N'-dimethyl-ethylenediamine monohydrochloride as a white crystalline solid (4.99 g, 45%). m.p. 108-110°C.  $\delta_H$  (400MHz; methanol-d<sub>4</sub>) 3.60 (2H, br m),  $\underline{CH_2}N(CH_3)$ ; 3.20 (2H, t, J 6.25 Hz),  $\underline{CH_2}NH(CH_3)$ ; 2.92 (3H, s),  $NCH_3$ ; 2.75 (3H, s),  $HNCH_3$ ; 1.47 (9H, s),  $C(CH_3)_3$ .  $\delta_C$  (75.4MHz; methanol-d<sub>4</sub>) 157.83, C=O; 81.52  $\underline{C}(CH_3)_3$ ; 48.43,  $NH(\underline{CH_3})$ ; 46.26,  $\underline{CH_2}NH(CH_3)$ ; 35.32,  $\underline{CH_2}NH(CH_3)$ ; 33.97,  $NCH_3$ ; 28.68,  $C(\underline{CH_3})_3$ . Found:  $M^+$  224.75.

The intermediate N-t-BOC, N, N'-dimethyl-ethylenediamine monohydrochloride (5.0 mmol, 1.12g) was stirred with 2M NaOH (11cm<sup>3</sup>) at room temperature for 10 min. The solution was then cooled to 0/C, and to this, was added a solution of acryloyl chloride (5.5 mmol, 0.45cm<sup>3</sup>) in chloroform (11 cm<sup>3</sup>), dropwise, over 30 min. After the addition was complete, the reaction mixture was stirred at 0/C for a further 1 h. The organic and aqueous phases were then separated, and the aqueous phase extracted with chloroform. The organic extracts were combined, dried (MgSO<sub>4</sub>), filtered and conc. *in vacuo*, to give the crude product. The crude product was stirred at room temperature over a slurry of basic alumina in

chloroform for 18 hr. Removal of the alumina and concentration of the filtrate then gave a pale yellow oil. Purification by flash chromatography (silica gel, diethyl ether : hexane : methanol elution) afforded N-t-BOC, N'-acryloyl, N, N'-dimethyl-ethylenediamine as a yellow oil (0.62g, 51%).  $\delta_H$  (300MHz;  $CDCl_3$ ) 6.56 (1H, dd, J 16.8, 10.4 Hz),  $\underline{CH}=\underline{CH}_aH_b$ ; 6.35 (1H, d, J 15.0 Hz),  $\underline{CH}=\underline{CH}_aH_b$ ; 5.67 (1H, d, J 10.3 Hz),  $\underline{CH}=\underline{CH}_aH_b$ ; 3.55 (2H, br m),  $\underline{CH}_2$ ; 3.37 (2H, m),  $\underline{CH}_2$ ; 3.07 (3H, m), N( $\underline{CH}_3$ ); 2.86 (3H, m), N( $\underline{CH}_3$ ); 1.45 (9H, m), C( $\underline{CH}_3$ )<sub>3</sub>.  $\delta_C$  (75.4MHz;  $CDCl_3$ ) 166.26,  $\underline{NOCHC}=\underline{CH}_2$ ; 155.57,  $\underline{NCO}_2C(\underline{CH}_3)_3$ ; 127.77,  $\underline{HC}=\underline{CH}_2$ ; 126.89,  $\underline{HC}=\underline{CH}_2$ ; 79.23,  $\underline{C}(\underline{CH}_3)_3$ ; 47.77,  $\underline{CH}_2N(\underline{CH}_3)OCHC=\underline{CH}_2$ ; 46.82,  $\underline{CH}_2N(\underline{CH}_3)CO_2C(\underline{CH}_3)_3$ ; 35.87,  $\underline{CH}_2N(\underline{CH}_3)OCHC=\underline{CH}_2$ ; 34.54,  $\underline{CH}_2N(\underline{CH}_3)CO_2C(\underline{CH}_3)_3$ ; 28.22, C( $\underline{CH}_3$ )<sub>3</sub>. Found:  $M^+$  242.34.

N-t-BOC, N'-acryloyl, N, N'-dimethyl-ethylenediamine (2.0 mmol, 0.46 g) was stirred in a solution of 3M HCl in ethyl acetate (2 cm<sup>3</sup>) at room temperature for 30 min. The solution was then conc. *in vacuo* to give N'-acryloyl, N, N'-dimethyl-ethylenediamine monohydrochloride as a clear yellow oil. This intermediate was stirred at room temperature in 2M NaOH (3 cm<sup>3</sup>) for 10 min. The reaction mixture was then cooled to 0°C, and to this, was then added a solution of methacryloyl chloride (2.2 mmol, 0.22 cm<sup>3</sup>) in chloroform (5 cm<sup>3</sup>) dropwise, over 30 min. After the addition was complete, the reaction mixture was stirred at 0°C for a further 1 h. The organic and aqueous phases were then separated, and the aqueous phase extracted with chloroform. The organic extracts were combined, dried (MgSO<sub>4</sub>), filtered and conc. *in vacuo*, to give the crude product. The crude product was stirred at room temperature over a slurry of basic alumina in chloroform for 18 hr. Removal of the alumina and concentration of the filtrate then gave a pale yellow oil. Purification by flash chromatography (silica gel, diethyl ether : hexane : methanol elution) afforded N-acryloyl, N'-methacryloyl, N, N'-dimethyl-ethylenediamine as a yellow oil (0.12g, 28%).  $\delta_H$  (300MHz;  $CDCl_3$ ) 6.49 (1H, dd, J 16.8, 10.4 Hz),  $\underline{HC}=\underline{CH}_aH_b$ ; 6.26 (1H, d, J 16.5),  $\underline{HC}=\underline{CH}_aH_b$ ;

5.66 (1H, m),  $\text{HC}=\underline{\text{CH}}_a\text{H}_b$ ; 5.12 (1H, br m),  $(\text{H}_3\text{C})\text{C}=\underline{\text{CH}}_c\text{H}_d$ ; 4.92 (1H, br m),  $(\text{H}_3\text{C})\text{C}=\underline{\text{CH}}_e\text{H}_f$ ; 3.53 (4H, br m), 2 x  $\underline{\text{CH}}_2$ ; 3.05 (3H, m)  $\text{N}(\underline{\text{CH}}_3)$ ; 2.98 (3H, m)  $\text{N}(\underline{\text{CH}}_3)$ ; 1.85 (3H, m),  $\underline{\text{CH}}_3$ .  $\delta_{\text{C}}$  (75.4MHz;  $\text{CDCl}_3$ ) 170.92,  $\text{NO}\underline{\text{C}}(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 165.04,  $\text{NO}\underline{\text{C}}\text{HC}=\text{CH}_2$ ; 139.39,  $(\text{H}_3\text{C})\underline{\text{C}}=\text{CH}_2$ ; 130.92,  $\text{HC}=\underline{\text{C}}\text{H}_2$ ; 126.01,  $\text{HC}=\text{CH}_2$ ; 119.56,  $(\text{H}_3\text{C})\text{C}=\underline{\text{C}}\text{H}_2$ ; 43.23,  $\underline{\text{CH}}_2\text{CH}_2$ ; 43.09,  $\text{CH}_2\underline{\text{C}}\text{H}_2$ ; 36.21,  $\text{N}(\underline{\text{CH}}_3)$ ; 35.47,  $\text{N}(\underline{\text{CH}}_3)$ ; 19.24,  $\underline{\text{C}}\text{H}_3$ . Found:  $\text{M}^+$  210.29.

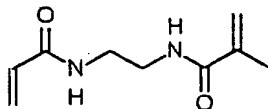
#### Method (b)

The intermediate N-t-BOC, N, N'-dimethyl-ethylenediamine monohydrochloride (5.0 mmol, 1.12g) as prepared above was stirred with 2M NaOH (11  $\text{cm}^3$ ) at room temperature for 10 min. The solution was then cooled to 0°C, and to this, was added a solution of methacryloyl chloride (5.5 mmol, 0.55  $\text{cm}^3$ ) in chloroform (11  $\text{cm}^3$ ), dropwise, over 30 min. After the addition was complete, the reaction mixture was stirred at 0°C for a further 1 h. The organic and aqueous phases were then separated, and the aqueous phase extracted with chloroform. The organic extracts were combined, dried ( $\text{MgSO}_4$ ), filtered and conc. *in vacuo*, to give the crude product. The crude product was stirred at room temperature over a slurry of basic alumina in chloroform for 18 hr. Removal of the alumina and concentration of the filtrate then gave a pale yellow oil. Purification by flash chromatography (silica gel, diethyl ether : hexane : methanol elution) then afforded N-t-BOC, N'-methacryloyl, N, N'-dimethyl-ethylenediamine as a pale yellow oil (0.82g, 64%).  $\delta_{\text{H}}$  (300MHz;  $\text{CDCl}_3$ ) 5.16 (1H, br m),  $(\text{H}_3\text{C})\text{C}=\underline{\text{CH}}_a\text{H}_b$ ; 5.00 (1H, br m),  $(\text{H}_3\text{C})\text{C}=\underline{\text{CH}}_c\text{H}_d$ ; 3.47 (4H, br m), 2 x  $\underline{\text{CH}}_2$ ; 3.04 (3H, m),  $\text{N}(\underline{\text{CH}}_3)$ ; 2.87 (3H, m),  $\text{N}(\underline{\text{CH}}_3)$ ; 1.93 (3H, br m),  $\underline{\text{CH}}_3$ ; 1.43 (9H, s),  $\text{C}(\underline{\text{CH}}_3)_3$ .  $\delta_{\text{C}}$  (75.4MHz;  $\text{CDCl}_3$ ) 172.22,  $\text{NO}\underline{\text{C}}(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 155.21,  $\text{N}\underline{\text{C}}\text{O}_2\text{C}(\text{CH}_3)_3$ ; 140.42,  $(\text{H}_3\text{C})\underline{\text{C}}=\text{CH}_2$ ; 115.21,  $(\text{H}_3\text{C})\text{C}=\underline{\text{C}}\text{H}_2$ ; 79.01  $\underline{\text{C}}(\text{CH}_3)_3$ ; 47.73,  $\underline{\text{CH}}_2\text{N}(\text{CH}_3)\text{OC}(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 44.99,  $\underline{\text{CH}}_2\text{N}(\text{CH}_3)\text{CO}_2\text{C}(\text{CH}_3)_3$ ; 36.94,  $\text{CH}_2\text{N}(\underline{\text{C}}\text{H}_3)\text{OC}(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 34.46,  $\text{CH}_2\text{N}(\underline{\text{C}}\text{H}_3)\text{CO}_2\text{C}(\text{CH}_3)_3$ ; 28.15,  $\text{C}(\underline{\text{C}}\text{H}_3)_3$ ; 20.15,  $\underline{\text{C}}\text{H}_3$ . Found:  $\text{M}^+$  256.37.



N-t-BOC, N'-methacryloyl, N, N'-dimethyl-ethylenediamine (2.0 mmol, 0.51 g) was stirred in a solution of 3M HCl in ethyl acetate (2 cm<sup>3</sup>) at room temperature for 30 min. The solution was then conc. in vacuo to give N'-methacryloyl, N, N'-dimethyl-ethylenediamine monohydrochloride as a clear yellow oil. This intermediate was stirred at room temperature in 2M NaOH for 10 min. The reaction mixture was then cooled to 0°C, and to this, was then added a solution of acryloyl chloride (2.2 mol, 0.18 cm<sup>3</sup>) in chloroform (5 cm<sup>3</sup>) dropwise, over 30 min. After the addition was complete, the reaction mixture was stirred at 0°C for a further 1 h. The organic and aqueous phases were then separated, and the aqueous phase extracted with chloroform. The organic extracts were combined, dried (MgSO<sub>4</sub>), filtered and conc. *in vacuo*, to give the crude product. The crude product was stirred at room temperature over a slurry of basic alumina in chloroform for 18 hr. Removal of the alumina and concentration of the filtrate then gave a pale yellow oil. Purification by flash chromatography (silica gel, diethyl ether : hexane : methanol elution) afforded N-acryloyl, N'-methacryloyl, N, N'-dimethyl-ethylenediamine as a yellow oil (0.20g, 47%). (Spectroscopic data as above)

**Example 8: Preparation of N-Acryloyl, N'-methacryloyl-ethylenediamine**



A solution of ethylenediamine (15 mmol, 10.1 cm<sup>3</sup>) in water (150 cm<sup>3</sup>) at 0°C was adjusted to pH 8.5 with 3N HCl. To this, was added a solution of methacryloyl chloride (16.5 mmol, 16.1 cm<sup>3</sup>) in chloroform (100 cm<sup>3</sup>), dropwise, over 2 h. After the addition was complete, the reaction mixture was stirred at 0°C for a further 2 h. The organic and aqueous layers were then separated, and the aqueous layer extracted with chloroform (3 x 50 cm<sup>3</sup>). The aqueous layer was then collected and conc. *in vacuo* (freeze-dryer)

to give a white solid. The residue was subjected to repeated fractional recrystallization from room temperature methanol, and the filtrate concentrated to give N-methacryloyl-ethylenediamine monohydrochloride as a clear, yellow oil (14.32 g, 58%). N-methacryloyl-ethylenediamine monohydrochloride (16 mmol, 20.0 g) was stirred in 2M NaOH (60 cm<sup>3</sup>) for 10 min. This solution was subsequently diluted to a volume of 160 cm<sup>3</sup> with water, and stirred at 0°C. To this mixture was added a solution of acryloyl chloride (17.6 mmol, 14.3 cm<sup>3</sup>) in chloroform (300 cm<sup>3</sup>), dropwise, over 3 h. After the addition was complete, the reaction mixture was then stirred at 0°C for a further 2 h. The organic and aqueous layers were separated, and the aqueous portion extracted with chloroform (3 x 100 cm<sup>3</sup>). The organic extracts were combined and concentrated to give the crude product as a white solid. Recrystallization from acetonitrile then gave N-acryloyl, N'-methacryloyl-ethylenediamine as colorless needles (10.70 g, 37%), m.p. 140-142/C.  $\delta_{\text{H}}$  (400MHz; CDCl<sub>3</sub>) 6.84 (1H, br s),  $\text{NH}$ ; 6.74 (1H, br m),  $\text{NH}$ ; 6.27 (1H, dd, J 16.9, 1.5 Hz),  $\text{HC}=\text{CH}_n\text{H}_b$ ; 6.13 (1H, dd, J 17.0, 10.2),  $\text{HC}=\text{CH}_a\text{H}_b$ ; 5.74 (1H, s),  $(\text{H}_3\text{C})\text{C}=\text{CH}_c\text{H}_d$ ; 5.65 (1H, dd, J 10.3, 1.6 Hz),  $\text{HC}=\text{CH}_a\text{H}_b$ ; 5.34 (1H, br m),  $(\text{H}_3\text{C})\text{C}=\text{CH}_e\text{H}_d$ ; 3.49 (4H, m), 2 x  $\text{CH}_2$ ; 1.95 (3H, s),  $\text{CH}_3$ .  $\delta_{\text{C}}$  (75.4 MHz; CDCl<sub>3</sub>) 169.4,  $\text{NHOC}(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 167.0,  $\text{NHOC}\text{HC}=\text{CH}_2$ ; 139.2,  $(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 130.7,  $\text{HC}=\text{CH}_2$ ; 126.2,  $\text{HC}=\text{CH}_2$ ; 120.1,  $(\text{H}_3\text{C})\text{C}=\text{CH}_2$ ; 40.4,  $\text{CH}_2\text{CH}_2$ ; 39.5,  $\text{CH}_2\text{CH}_2$ ; 18.4,  $\text{CH}_3$ . Found:  $\text{M}^+$  182.1059.

#### Example 9: Preparation of monomer stock solutions and SDS gels.

This example describes a general procedure for preparing stock solutions of acrylamide with a desired crosslinking agent. To ensure that the degree of crosslinking is equivalent to the corresponding acrylamide/BIS systems the amount of crosslinking agent is calculated on a mole:mole basis rather than a weight:weight basis.

1. Prepare monomer stock solutions of the following concentrations depending on the desired crosslinking agent concentration.

a) 30%T 3%C Dissolve 29.1g acrylamide and  $5.837 \times 10^{-3}$  moles of crosslinking agent (equivalent to 0.9g of BIS on a mole:mole basis) in 50ml of distilled water and bring to a total volume of 100ml.

b) 30%T 6%C Dissolve 28.2g acrylamide and  $11.67 \times 10^{-3}$  moles of crosslinking agent (equivalent to 1.80g of BIS) in 50ml of distilled water and bring to a total volume of 100ml.

2. Filter monomer solution through Whatman No. 1 filter paper.

Monomer stock solution may be stored at 40°C for 2 to 3 months.

3. To the required amounts of water and 1.5M Tris HCl buffer are added the required aliquots of the 30%T monomer stock solution of the desired °C ratio (see Table 2, this being an example of the concentration range employed). Degas monomer solution under vacuum for 10 min at room temperature and then 10 min at 10°C.

4. Add 10% SDS solution, and then redox initiator system composed on freshly prepared 10% ammonium persulfate (10% AP, 200  $\mu$ l / ml) and 3-dimethylaminopropionitrile (DMAPN, 5  $\mu$ l / ml, except for 5%T 3%C stacking gel which is 10  $\mu$ l/ml) to monomer solution and swirl gently to mix.

**Table 2**

ITEM	5%T	10%T	15%T
water	16.6 ml	11.6 ml	6.6ml
1.5 M Tris buffer (pH 8.8)	7.5 ml	7.5 ml	7.5 ml
acrylamide / monomer stock	5.0 ml	10.0 ml	15.0 ml
10% SDS	0.300 ml	0.300 ml	0.300 ml
10% ammonium persulfate	0.600 ml	0.600 ml	0.600 ml
DMAPN	30 $\mu$ l	15 $\mu$ l	15 $\mu$ l
TOTAL VOLUME	30 ml	30 ml	30 ml

5. Using a syringe, inject resolving gel solution slowly into prepared glass cassettes to a height of 75 mm, which are prepared as follows:

5 Glass cassettes are thoroughly cleaned with detergent and then allowed to air dry before being swabbed with ethanol or iso-propanol to remove any grease or detergent film, and also to neutralise the surface of the glass. After cleaning, the sides and base of the cassettes are taped up using 3M Scotch electrical tape and then placed in a 60°C oven for 1 hr.

10 The polyacrylamide gel is allowed to form (approx. 30 to 45 min) under an atmosphere of nitrogen. This nitrogen atmosphere is used for the polymerization procedure to ensure the absence of oxygen, thereby eliminating the appearance of "swirls" or "troughs" on polymerization.

6. Slowly apply a 5%T 3%C stacking gel onto the top of the resolving gel, which is also allowed to polymerize under an atmosphere of nitrogen.

15 7. Carefully remove the tape and wash the cassettes under water. Gels are then ready for electrophoresis. By this method it is possible to prepare vast range and size of well polymerized and optically transparent gels by varying the proportions of water and acrylamide /crosslinking agent stock solution.

#### 20 **Example 10: SDS-PAGE**

This example describes a general procedure for performing SDS-PAGE with gels prepared in accordance with the invention.

1. Use a white surface when applying samples to the gels.

25 2. Insert gels into electrophoresis kit (which has been assembled according to manufacturers' instructions) and fill both reservoirs in the kit with SDS-PAGE running buffer or appropriate buffer. Place sample wells into the stacking gel at a depth of 1-2 mm.

3. Blow out any air bubbles appearing in the sample wells from above, using a plastic pipette.

4. Load approx. 10 $\mu$ l of sample (eg. peptide or DNA marker) into the sample well using a microsyringe. Sample should "sit" nicely inside the well and be an intense blue colour. If too much sample is added, surrounding solution will go cloudy as the sample overflows from the well.

5. Electrophoresis is then performed noting that a 200V is maintained. current is between 150-40mA and the process performed for the required time (60 minutes to days). The experiment is complete when the dye front reaches the bottom of the plate.

6. Remove sample spacers from the gel after approx. 2 min.

7. When electrophoresis is complete, the gel cassette may be removed and opened, and the gel eased off the cassette under running water.

8. The gel is washed into a vessel containing Coomassie Blue R-250 (0.25% coomassie blue, 40% methanol, 10% acetic acid) and stained for at least 30 min for proteins or ethidium bromide for DNA under known of the art conditions.

9. Gel is then destained (for proteins) by soaking in 40% methanol, 10% acetic acid overnight.

10. Gel is then sealed in to zip-lock bag, labelled and filed eg. in plastic pockets of a folder for reference.

#### **Example 11: Comparison of electrophoretic performance with standard BIS/acrylamide gels**

In this example the performance of gels prepared in accordance with the present invention is compared to the performance of standard BIS/acrylamide gels. For the purpose of the comparison the asymmetrical crosslinking agents were substituted for BIS on a mole:mole basis rather than on a weight:weight basis to ensure equivalence in the number of reactive double bonds. The gels were compared by examining the migration velocity ( $R_f$ ) of peptide and DNA markers in the respective gels, where  $R_f$  is defined as:

$$R_f = \frac{\text{distance migrated by protein or DNA}}{\text{distance travelled by dye front}}$$

a) **Preparation of acrylamide/crosslinking agent stock solution**

5 Stock solutions of acrylamide and the crosslinking agents were prepared to provide acrylamide/crosslinking agent stock solutions equivalent (on a mole:mole basis) with a 30%T 3%C acrylamide/BIS solution:

for BIS (Gel A);

10 29.1g of acrylamide and 0.90g ( $5.837 \times 10^{-3}$  moles) of crosslinking agent;

for N-acryloyl, N'-methacryloyl methylenediamine (Gel B);

29.1g of acrylamide and 0.98g ( $5.837 \times 10^{-3}$  moles) of crosslinking agent;

15 for N-acryloyl, N'-methacryloyl ethylenediamine (Gel C);

29.1g of acrylamide and 1.06g ( $5.837 \cdot 10^{-3}$ ) moles of crosslinking agent; and

for methacrylethylacrylamide (Gel D);

20 29.1g of acrylamide and 1.07g ( $5.837 \times 10^{-3}$  moles) of crosslinking agent.

b) **Preparation of gels**

Gels were prepared from the stock solutions in accordance with Table 3 below.

Table 3

Major Components	10%T 3%C*	15%T 3%C*
Water	11.6 ml	6.6 ml
1.5M Tris Buffer pH 8.8	7.5 ml	7.5 ml
Stock Solution	10.0 ml	15.0 ml
10% SDS	0.300 ml	0.300 ml
10% ammonium persulfate	0.600 ml	0.600 ml
DMAPN	15 $\mu$ l	15 $\mu$ l
Total Volume	30 ml	30 ml

\* These weight based concentrations of acrylamide and crosslinking agent are only correct when BIS is employed as the crosslinking agents. When a crosslinking agent other than BIS is employed, the amount of crosslinking agent is the mole:mole equivalent of BIS required to give these concentrations.

c) **Assessment of electrophoretic performance**

The stained gels shown in figures 1 and 2 were obtained after performing electrophoresis under the standard conditions with a commercially available standard molecular weight protein marker system composed of (1) myosin (200,000), (2),  $\beta$ -galactosidase (116,250), (3) phosphorylase b (97,400), (4) bovine serum albumin (66,200), (5) ovalbumin (45,000), (6) carbonic anhydrase (31,000), (7) soybean trypsin inhibitor (21,5000), (8) lysozyme (14,400) and (9) aprotinin (6,500). The gels contain the following crosslinking gents: (Gel A) methylene-bisacrylamide (BIS), (Gel

B) N-acryloyl, N'-methacryloyl methylenediamine, (Gel C) N-acryloyl, N'-methacryloyl ethylenediamine and (Gel D) 2-methacrylethylacrylamide.

(i) 10%T 3%C gels

The 10%T 3%C gels prepared and stained as described above are shown in figure I. It is clear from a comparison of the stained gels that equivalent proteins move through the gels incorporating the asymmetrical crosslinking agents (Gels B, C and D) at a faster rate, ie. have a higher migration or Rf value, than through the standard BIS gel (Gel A).

There also appears to be differences in the degree of separation between specific protein bands such that these new gels may be used in a manner to achieve a maximum of separation and resolution within a particular molecular weight region. For example, a 10%T 3%C gel incorporating N-acryloyl, N'-methacryloyl methylenediamine (Gel B) exhibits an improved separation for the protein bands in the region 116,250 to 66,200, which is similarly observed for the Gels C and D. Each of Gels B, C and D showed enhanced performance in the separation of the high molecular weight components of the marker system, while remaining optically transparent.

(ii) 15%T 3% gels

The 15%T 3%C gels prepared and stained described above are shown in figure 2.

As with the 10%T 3% gels described above, these 15%T 3%C gels incorporating asymmetrical crosslinking agents (Gels B, C and D) afforded improved electrophoretic separations compared to the BIS gel (Gel A). The improved separation is evident for both the high and low molecular weight components.

These results show an enhanced separation and improved resolution, while still maintaining optical transparency. For example, the 15%T 3%C gel incorporating the crosslinking agent N-acryloyl, N'-methacryloyl methylenediamine (Gel B) exhibits an enhanced separation in the region



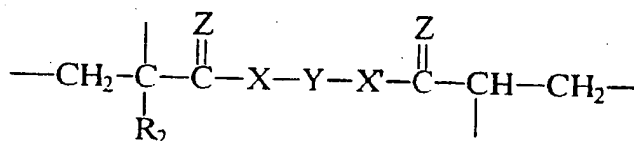
66,000 to 21,500. Similar results are observed for the gels containing the other asymmetrical crosslinking agents (Gels C and D).

5 Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A crosslinked polymer gel comprising a crosslinking moiety of the formula:



wherein X and X' are independently selected from the group consisting of -O-, -S- and -NR-, where R is H, alkyl or cycloalkyl.

Y is an optionally substituted non-aromatic divalent linking group,

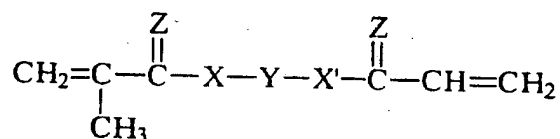
Z is O or S; and

R<sub>2</sub> is a C<sub>1</sub>-C<sub>4</sub> alkyl group.

2. A crosslinked polymer gel according to claim 1 wherein R<sub>2</sub> is CH<sub>3</sub>.

3. A crosslinked polymer gel according to claim 1 or claim 2, wherein the crosslinked polymer gel is a polymer or copolymer of acrylamide, an acrylamide derivative and/or an acrylamide substitute and optionally one or more other comonomers.

4. A crosslinked polymer gel according to any one of the preceding claims wherein the gel is an aqueous gel comprising the product formed by crosslinking polymerisation of one or more monomers selected from compounds of the formula H<sub>2</sub>C=CR<sub>5</sub>-CO-NR<sub>3</sub>R<sub>4</sub> where R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are each independently selected from H or optionally substituted alkyl, and one or more crosslinking agents of the formula:



where X and X' are selected from the group consisting of -O-, -S- and -NR-, where R is H, alkyl or cycloalkyl,

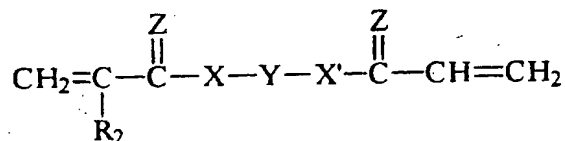
Y is an optionally substituted non aromatic divalent linking group,  
and Z is O or S.

5. A gel according to any one of the preceding claims wherein the  
divalent linking group is selected from the group alkylene, oxyalkylene,  
polyoxyalkylene, cycloalkylene, alkanedioyl, alkylendisulphonyl,  
alkylenecarbonyl, thioalkylene, ureylene, oxalyl, aminoalkylene,  
alkylendisulphonyl, heterocyclyl and groups of the formula  $-(R^1)_m-R^2-(R^3)_n-$ ,  
where  $R^1$  and  $R^3$  are selected from alkylene, cycloalkylene, heterocyclyl,  
oxyalkylene, polyoxyalkylene, alkylenecycloalkylene and  
alkyleneheterocyclyl;  $R^2$  is selected from a direct bond, -O-, -S-, -S-S-,  
alkylene, alkanedioyl, alkylendioxy, alkylendisulphonyl, -NR-, -NRC(O)O-,  
-NR-C(O)-NR-, -NRC(O)-, -N=N-, -NRC(O)C(O)-NR-, -C(O)-, -C(S)- and -  
RNNR-, where R is H, alkyl or cycloalkyl; m and n are 0 or 1 provided that m  
+ n  $\neq$  0.

6. A porous electrophoretic medium comprising a gel in accordance  
with any one of the preceding claims.

7. An electrophoretic medium according to claim 6 wherein the  
electrophoretic medium has a porosity gradient.

8. A method of preparing a crosslinked polymer gel, the method  
including the step of subjecting one or more monomers to crosslinking  
polymerisation with one or more crosslinking agents of formula :



wherein X and X' are independently selected from the group  
consisting of -O-, -S- and -NR-,

where R is H, alkyl or cycloalkyl,

$\text{R}_2$  is a  $\text{C}_1$ - $\text{C}_4$  alkyl group,

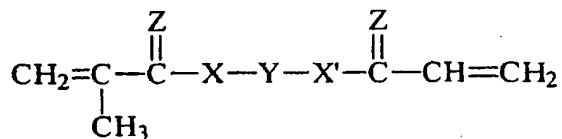
Y is an optionally substituted non aromatic divalent linking group,  
and Z is O or S.

9. A method according to claim 8 wherein the polymer gel is formed by crosslinking polymerisation of one or more crosslinking agents of formula I, optionally in the presence of one or more conventional crosslinking agents.

10. A method according to claims 8 or 9 wherein X and X' are the same and R<sub>2</sub> is CH<sub>3</sub>.

11. A method according to any one of claims 8 to 10 wherein the crosslinked polymer gel is an aqueous gel comprising the product formed by crosslinking polymerisation in the presence of an aqueous medium of one or more monomers selected from the formula H<sub>2</sub>C=CH-CO-NR<sub>3</sub>R<sub>4</sub> wherein R<sub>3</sub> and R<sub>4</sub> are each independently H or alkyl optionally mono-substituted with OH or C(O)CH<sub>2</sub>C(O)CH<sub>3</sub>, optionally one or more other comonomers and one or more cross-linking agents selected from compounds of formula I.

12. A compound of formula:

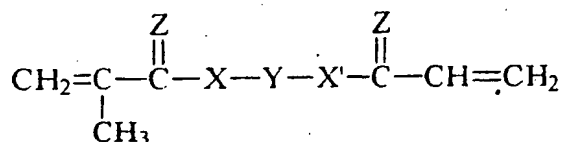


wherein X and X' are selected from -S- and -NR-, where R is H, alkyl or cycloalkyl, and

Y is an optionally substituted non aromatic divalent linking group, and

Z is O or S, provided that when X and X' are both -NR-, Y is not -CH<sub>2</sub>- and does not include a quaternary ammonium group.

13. A compound of formula :



wherein one of X and X' is -O- and the other is selected from -S- and -NR-, where R is H, alkyl or cycloalkyl, and

Y is an optionally substituted non aromatic divalent linking group,  
and

Z is O or S;

provided that Y is not C<sub>1-5</sub> alkylene and does not include a quaternary ammonium group, and that when the other of X and X' is -NH-, Y is not methyleneoxy -2- hydroxypropylene.

14. A polymer gel according to any one of claims 1 to 5 wherein the polymer gel is formed by crosslinking polymerisation of one or more compounds according to claim 12 or claim 13.

15. A method of separating molecules comprising providing a crosslinked polymer gel according to any one of claims 1 to 14, placing a sample containing the molecules to be separated onto the gel, and subjecting the gel and sample to a separation technique.

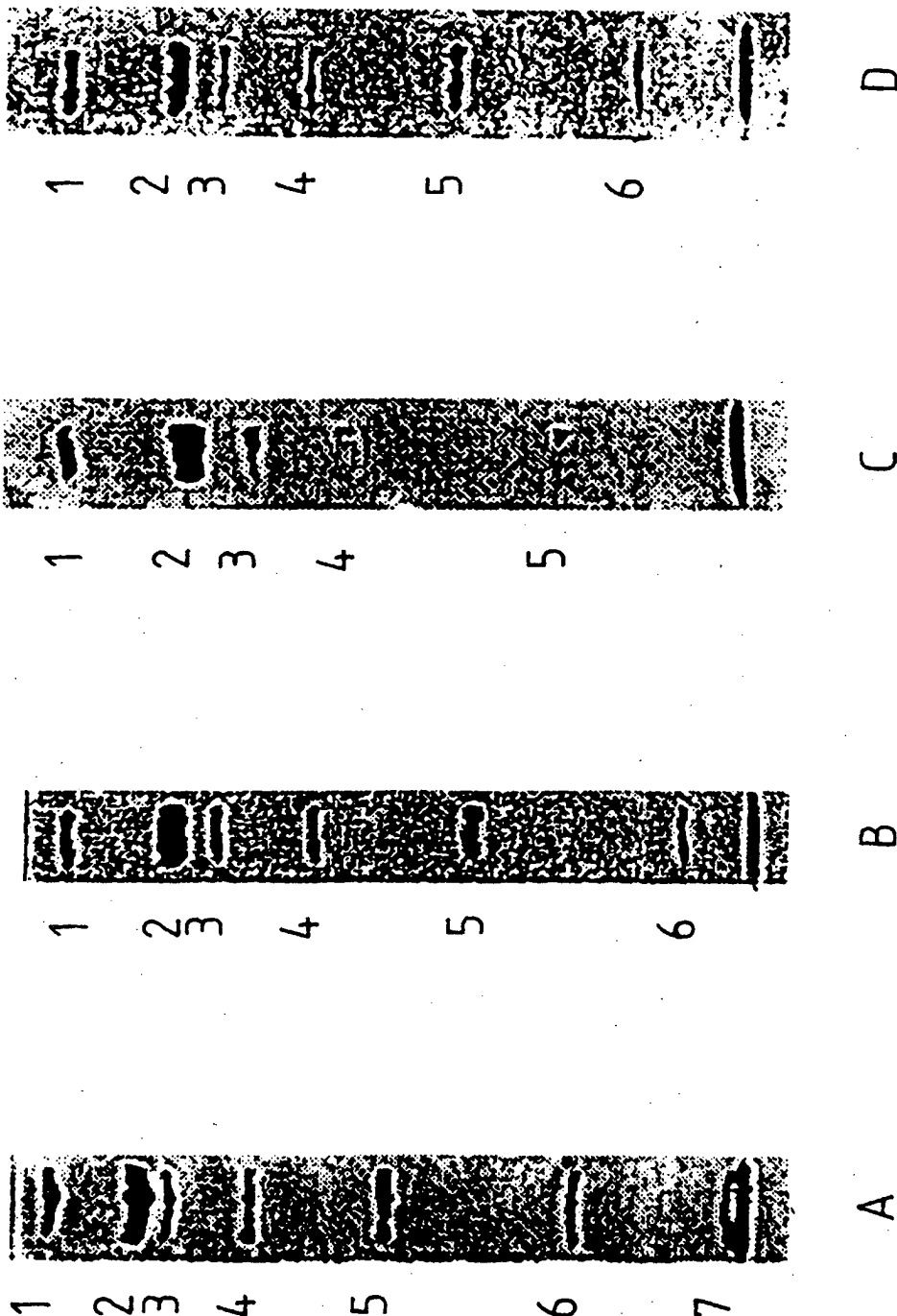
16. A method according to claim 11 wherein the separation technique is electrophoresis.

17. A method according to claim 15 or 16 wherein the sample includes a biomolecule selected from proteins, enzymes, peptides, oligo- or polynucleotides and carbohydrates.

18. A crosslinked polymer formed from one or more monomers and one or more compounds in accordance with claim 12 or claim 13.

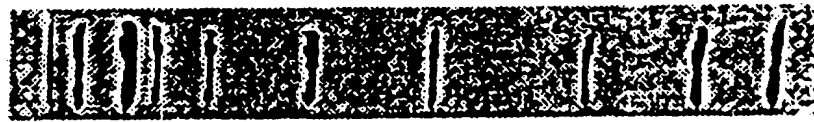
1/2

FIG 1



2/2

FIG 2



1 2 3 4 5 6 7 8 9

D



1 2 3 4 5 6 7 8 9

C



1 2 3 4 5 6 7 8 9

B



1 2 3 4 5 6 7 8 9

A

## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/AU 97/00437

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
Int Cl <sup>6</sup> : C07C 233/20, 233/38 CO8F 220/56, 246/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CAS on line: substructure search		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 300 537 A (Müller et al.) 05 April 1994 Column 1 lines 1-60	13
X	Chemical Abstracts, Abstract No. 99: 128392, JP 58 028 718 A2 (Toyo Contact Lens Co., Ltd) 19 February 1983 Abstract	1-3
X	Chemical Abstracts, Abstract No. 99:54494, JP 58 029 744 A2 (Toyo Contact Lens Co., Ltd) 22 February 1983 Abstract	1-3
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
• Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 30 July 1997		Date of mailing of the international search report <b>06 AUG 1997</b>
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (06) 285 3929		Authorized officer  <b>GAYE HOROBIN</b> Telephone No.: (06) 283 2069



## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 97/00437

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 417 034 A (WEBSTER) 22 November 1983 Example 36	1-3
A	AU 40206/95 A (IVOCLAR AG) 13 June 1996 Whole document	1-3
A	EP 510 646 A (FUJI PHOTO FILM CO., LTD) 28 October 1992 Whole document	1-3

### Information on patent family members

**PCT/AU 97/00437**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	5 300 537	AT	106 862	AU	53725/90	CA	2 015 438
		DE	3 913 939	EP	394 787	ES	2 055 209
		IE	64 131	JP	3 204 846	PT	93 874
EP	510 646	DE	69 203 642	EP	510 646	JP	4 324 865
US	4 417 034	AR	241 118	AT	22450	AT	53593
		AU	85442/82	BR	8 203 809	CA	1 186 435
		DE	3 272 440	DE	3 280 190	DK	2926/82
		EP	68887	ES	513 604	GB	2 102 818
		HK	479/87	HK	804/90	JP	58 013 603
		JP	5 079 685	KR	8 904 083	NO	822 230
		SG	223/87	SG	673/90	ZA	8 204 678
		ZW	132/82	US	4 508 880	US	4 681 918
		US	4 711 942	US	4 783 500		
EP	510 646	DE	69 203 642	EP	510 646	JP	4 324 865
AU	95/40206	CA	2 164 175	DE	4 443 702	EP	716 103
		JP	8 231 864				

END OF ANNEX

performed by nuclear magnetic resonance (NMR) analysis, and is described in more detail below.

In one preferred embodiment, the basestock that forms a primary component of the lubricating oils of the present invention comprises a novel hydrocarbon composition described in co-pending Serial No. 09/170,683, corresponding to international publication number WO 99/20720, incorporated herein by reference. In a preferred embodiment, the hydrocarbon composition is produced by the isomerization of Fischer Tropsch waxes. Accordingly, the basestocks may be referred to herein as wax isomerate basestocks, but are not necessarily limited to such basestocks, as any basestock meeting the compositions defined by equations (a) and (b) may be used. For example, while it is preferable to produce the liquid hydrocarbon basestocks used in the present invention from Fischer-Tropsch-derived raw materials, other waxy hydrocarbon materials, such as conventional waxy lube raffinates, slack waxes, deoiled slack waxes, foots oils and lube distillate hydrocrackates may be used to produce the primary hydrocarbon basestocks described in the present invention.

The process of making the lubricant oil basestocks of the present invention may be characterized as a hydrodewaxing process. The hydrodewaxing process may be conducted over a combination of catalysts, or over a single catalyst. Conversion temperatures may range from about 200°C to about 500°C at pressures ranging from about 500 to 20,000 kPa. This process is operated in the presence of hydrogen, and hydrogen partial pressures will normally be from 600 to 6000 kPa. The ratio of hydrogen to the hydrocarbon feedstock (hydrogen circulation rate) will normally be from 10 to 3500 n.l.l.<sup>-1</sup> (56 to 19,660 SCF/bbl) and the space velocity of the feedstock will normally be from 0.1 to 20 LHSV, preferably 0.1 to 10 LHSV.

Hydrocarbon conversion catalysts useful in the conversion of the waxy feedstocks disclosed herein to form the hydrocarbon components of the present invention are zeolite catalysts, such as ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-12, ZSM-38, ZSM-48, offretite, ferrierite, zeolite beta, zeolite theta, zeolite alpha, as disclosed in U.S. Patent no. 4,906,350. These catalysts are used in combination with Group VIII metals, in particular palladium or platinum. The Group VIII metals may be incorporated into the zeolite catalysts by conventional techniques, such as ion exchange.

In one preferred embodiment, conversion of the waxy feedstock may be conducted over a combination of Pt/zeolite beta and Pt/ZSM-23 catalysts in the presence of hydrogen. In another embodiment, the process of producing the lubricant oil basestocks comprises hydroisomerization and dewaxing over a single catalyst, such as Pt/ZSM-35. In either case, the unique products of the present invention may be obtained.

The resulting liquid hydrocarbon basestocks are conveniently characterized by pour point, one of several key physical and chemical properties described herein. Pour point may be measured according to ASTM method D97, Test Method for Pour Points of Petroleum Products, and is reported in °C. However, the preferred technique for pour point is the automated method ASTM D5950, Test Method for Pour Point of Petroleum Products (Automatic Tilt Method), with pour points reported in °C.

The liquid hydrocarbon basestocks of the present invention may have very low concentration levels of typical contaminants found in lube oil basestocks refined from natural mineral oils, depending upon the nature of the feedstock used to produce the liquid hydrocarbons. Typically, the liquid hydrocarbon compositions of the present invention have less than 0.1 wt%

aromatic hydrocarbons, less than 20 ppm by weight of nitrogen-containing compounds, less than 20 ppm by weight of sulfur-containing compounds and low levels of naphthenic hydrocarbons, *i.e.* cycloparaffins. The concentration levels of both sulfur and nitrogen compounds in these hydrocarbon compositions, when derived from Fischer Tropsch waxes, are preferably less than 10 ppm each, and more preferably less than 1 ppm each. Thus, it is preferred to produce the liquid hydrocarbon basestocks of the present invention from Fischer-Tropsch-derived materials in order to obtain the very low level of contaminants in the product fluids.

On average, the primary liquid hydrocarbon compositions of the present invention are paraffinic hydrocarbon components having fewer than 10 hexyl- or longer branches per 100 carbon atoms. The hydrodewaxing step used to produce the liquid hydrocarbons of the present invention results in significant levels of isomerization of the long chain paraffins in the waxy feedstocks, resulting in paraffinic hydrocarbon components with a plurality of branches, as described in formulas (a) and (b).

As noted above, the primary hydrocarbon basestocks of the present invention comprise a major component of the formulated lubricating oils of the present invention and may be used in combination with other lubricating oil basestocks, such as for example mineral oils, polyalphaolefins, esters, polyalkylenes, alkylated aromatics, hydrocrackates and solvent-refined basestocks.

The primary lubricant oil basestocks of the present invention contain primarily isoparaffinic components with nominal boiling points of 370°C or more and are unusual in that they unexpectedly exhibit a unique combination of both high viscosity indices and extremely low pour points. These two characteristics are generally known in the art to be related in direct proportion,

i.e., lowering the pour point of a hydrocarbon fluid results in decreasing the viscosity index, and therefore it is quite unusual to obtain both an extremely low pour point and a relatively high VI in the same fluid. For example, conventional mineral oil basestocks, such as Comparative Examples 3-5 herein, exhibit relatively low VI's when pushed into the low pour point ranges (Table 3).

However, the primary basestocks of the present invention are characterized by low pour points of less than or equal to  $-18^{\circ}\text{C}$ , preferably less than or equal to  $-25^{\circ}\text{C}$  and more preferably less than or equal to  $-30^{\circ}\text{C}$ , with kinematic viscosities (KV) ranging from about 2.0 cSt to greater than about 13 cSt, preferably about 4 cSt to about 10 cSt, at  $100^{\circ}\text{C}$  and high viscosity indices (VI) from about 120 to about 160, preferably from about 130 to about 160 and more preferably from about 140 to about 160, as well as BI and  $\text{CH}_2>4$  values as set forth in formulas (a) and (b), above.

In particular, preferred wax isomerate lubricant basestocks have a combination of VI and pour point from about 130 VI/ $-66^{\circ}\text{C}$  to about 160 VI/ $-20^{\circ}\text{C}$  and more preferably from about 140 VI/ $-55^{\circ}\text{C}$  to about 160 VI/ $-25^{\circ}\text{C}$ .

An upper VI limit of about 160 is particularly notable because as VI values increase beyond 160, the basestock's MRV viscosity begins rapidly increasing (Figure 4), and may reach levels which could render such basestocks unsuitable for formulating multi-grade engine oils. Waxy hydrocarbons in lube base stocks directly influence low-temperature lube properties, and MRV is significantly sensitive to waxiness, due to the long cooling cycle and the low-shear used by the test procedure. The presence of even small amounts of waxy hydrocarbons in the wax isomerate basestock can have a major negative impact on MRV viscosity and MRV yield stress (respectively, limits of 60000 cP max, and 35 Pa max).

An unexpected advantage was also found for finished oils formulated with wax-isomerate base oils having pour points in a range of approximately -30°C to about -45°C compared to base oils with pour points below about -45°C, for example about -60°C or lower, pour points. Note in Figure 4 that CCS viscosity unexpectedly increases as basestock pour point decreases, over the range of about -20°C to about -60°C and lower. At comparable wax isomerate base oil viscosity, a finished lube formulated with a wax isomerate base oil having a pour point from about -30°C to -45°C demonstrates a more beneficial, lower CCS viscosity than that of an analogous finished lube formulated with an isomerate base oil component having a pour point less than -45°C. For example, a comparison of Examples 18 and 17 (Table 13) using base oils B-1 (-34°C pour) versus A-2 (-49°C pour), respectively, shows that Example 18 achieves a lower and more advantageous CCS viscosity than Example 17. The lower CCS viscosity of the formulated lube containing the higher pour point base oil permits increased flexibility in achieving the industry targets which specify maximum permissible CCS viscosity limits for formulated oils according to viscosity grade.

Among the other advantages of this invention is the surprisingly good biodegradability of the primary base oils utilized in the present lubricating oil formulations, together with the combination of desirable low temperature properties they possess. Moreover, the formulated lubes derived from certain wax isomerate base oils can simultaneously exceed the blending (viscometric) flexibility of typical hydroprocessed base oils, as well as surpass the biodegradation performance of typical PAOs.

Wax isomerate base oil biodegradation was measured by both OECD 301B and CEC L-33-A-93 test methods. Both tests are described briefly below.

The OECD 301B modified Sturm CO<sub>2</sub> Test Method is a test method developed by the Organization for Economic Cooperation and Development and reported in "OECD Guidelines for the Testing of Chemicals," Vol. 2, Section 3, pp. 18-24 (Adopted July 17, 1992), and is incorporated herein by reference. This test measures the aerobic microbial biodegradation of a test material by its complete breakdown to carbon dioxide.

According to OECD 301B, in general, the biodegradability of a test material over a 28-day period is determined by measuring the evolution of carbon dioxide from the microbial oxidation of the test material's organic carbon. The carbon dioxide produced is trapped in barium hydroxide solution and is quantified by titration of residual hydroxide with standardized HCl. To determine the percent biodegradation, the amount of CO<sub>2</sub> produced microbially from the test material is compared to its theoretical carbon dioxide (the complete oxidation of the carbon in the test material to CO<sub>2</sub>). Positive controls, using sodium benzoate as reference material, are run to check the viability of the aerobic microorganisms used in the procedure. Blank controls are also run in parallel. Tests, controls, and blanks are run in duplicate.

The CEC L-33-A-93 Test Method is a test method developed by the Coordinating European Council (CEC) and reported in "Biodegradability of Two-Stroke Cycle Outboard Engine Oils in Water," 38 pages (issued February 21, 1995) and incorporated herein by reference. This test measures the decrease in the amount of the parent material due to microbial action.

According to CEC L-33-A-93, in general, primary biodegradability of a test material is determined as follows: an aqueous mineral medium solution and a known amount of the test material are incubated with an inoculum of



unacclimated aerobic microorganisms from sewage. The test material is the nominal sole source of carbon. The test system is incubated at a constant temperature with continuous agitation in the dark over a period of 21 days. A poisoned reference mixture containing mineral medium solution, the test material, and mercuric chloride (to inhibit microbial activity) is also run in parallel. Tests and references are done in triplicate. Primary biodegradation of the test material is determined by quantifying (via extraction, and infrared spectral analysis) the amount of unchanged parent material remaining at the end of 21 days.

The biodegradation characteristics of certain wax isomerate basestocks of the present invention are referenced in Table 9 below. These wax isomerate basestocks are significantly more biodegradable than the PAO lube basestocks. In addition, these same wax isomerate basestocks are generally more biodegradable than conventional hydroprocessed basestocks, as exemplified by the Shell XHVI and the Chevron UCBO oils.

The primary hydrocarbon basestocks utilized in the present formulations typically have a biodegradability of greater than 50% under the OECD 301B test, preferably about 60% or greater, and more preferably about 65% or greater.

The hydrocarbon basestocks of the present invention typically comprise from about 10 to about 99.5 wt% of the total formulation, preferably from about 40 to about 95 wt%, and more preferably from about 60 to about 90 wt%. It is to be recognized that the percentage of the wax isomerate basestocks in conjunction with the other lubricating oil components may be varied depending on the particular formulation performance requirements desired.

### OTHER LUBRICANT OIL COMPONENTS

In addition to the primary basestocks described above, the oil formulations of the present invention comprise numerous other components in order to achieve the desired combination of properties in the finished lubricant. The other lubricant oil components may comprise, without limitation, other optional base oils, performance polymers, viscosity modifier polymers, performance additives, and performance additive packages. The proper selection of these other components is important to impart the necessary characteristics associated with the various multigrade service requirements.

### OPTIONAL BASESTOCKS

For example, the lubricants of the present invention may comprise optional basestocks, such as mineral oils and, in particular, synthetic basestocks. The mineral-derived basestocks may include typical light neutral oils, and synthetic basestocks may include, for example, polyalpha olefins, alkyl aromatics and esters. Synthetic hydrocarbon basestocks are preferred, especially the PAOs with viscosities in the range of 1.5 to 12 cSt, generally with VI's of 120 or greater, either in the form of single component or blended PAOs. Optionally, other hydrocarbon basestocks (mineral-derived or synthetic) with high viscosity, up to 3000 cS or more at 100°C, may also be used. As alternatives, other synthetic basestocks may be used, for example, alkylbenzenes, and other alkylated aromatics such as alkylated naphthalene, alkylated diphenyl ethers, alkylated diphenyl sulfides, and alkylated diphenyl methanes, as well as the synthetic basestocks described in "*Synthetic Lubricants*," Gunderson and Hart, Reinhold Publ. Corp., New York 1962. Other alternatives may also include esters, for example, with mono-, di-, tri-, or tetra-carboxylate functionality.

The Poly Alpha Olefins (PAOs) typically comprise relatively low molecular weight hydrogenated polymers or oligomers of alphaolefins which include but are not limited to  $C_2$  to about  $C_{32}$  alphaolefins with  $C_8$  to about  $C_{16}$  alphaolefins, such as 1-octene, 1-decene, 1-dodecene, and the like, being preferred. The preferred polyalphaolefins are poly-1-decene and poly-1-dodecene, although the dimers of higher olefins in the range of  $C_{14}$  to  $C_{18}$  may be used to provide low viscosity basestocks of acceptably low volatility. The PAOs in the viscosity range of 1.5 to 12 cSt, are generally predominantly trimers and tetramers of the starting olefins, with minor amounts of the higher oligomers, depending on the exact viscosity grade and the starting oligomer.

The PAO fluids may be conveniently made by the polymerization of an alphaolefin in the presence of a polymerization catalyst, such as the Friedel-Crafts catalysts including, for example, aluminum trichloride, boron trifluoride or complexes of boron trifluoride with water, alcohols such as ethanol, propanol or butanol, carboxylic acids or esters such as ethyl acetate or ethyl propionate. For example the methods disclosed by U.S. 4,149,178 or U.S. 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the following U.S. Patents: 3,742,082 (Brennan); 3,769,363 (Brennan); 3,876,720 (Heilman); 4,239,930 (Allphin); 4,367,352 (Watts); 4,413,156 (Watts); 4,434,408 (Larkin); 4,910,355 (Shubkin); 4,956,122 (Watts); 5,068,487 (Theriot). The dimers of the  $C_{14}$  to  $C_{18}$  olefins are described in U.S. 4,218,330.

In addition, other basestocks may also be combined with the primary hydrocarbon basestocks defined in the present invention. For example, it may be desirable to utilize one or more other components which possess additional chemical functionality (e.g., aromatic, ester, ether, alcohol, etc.) in order to confer additional desired characteristics, such as, for example, additive solvency

and seal compatibility, to the finished lubricant. Certain additives used in oils contain aromatic groups, and for adequate solvency, some aromatic character in the basestock may be required, even though aromatics, generally, do not lead to optimum lubricant performance in themselves. In addition, additive solvency and seal compatibility characteristics may be secured by the use of ester basestocks.

In alkylated aromatic stocks, the alkyl substituents are typically alkyl groups of about 8 to 25 carbon atoms, usually from 10 to 18 carbon atoms and up to three such substituents may be present, as described for the alkyl benzenes in ACS Petroleum Chemistry Preprint 1053-1058, *"Poly n-Alkylbenzene Compounds: A Class of Thermally Stable and Wide Liquid Range Fluids"*, Eapen *et al.*, Phila. 1984. Tri-alkyl benzenes may be produced by the cyclodimerization of 1-alkynes of 8 to 12 carbon atoms as described in U.S. Pat. No. 5,055,626. Other alkylbenzenes are described in EP 168534 and U.S. Pat. No. 4,658,072. Alkylbenzenes have been used as lubricant basestocks, especially for low-temperature applications (e.g., Arctic vehicle service and refrigeration oils) and in papermaking oils; they are commercially available from producers of linear alkylbenzenes (LABs). The linear alkylbenzenes typically have good low pour points and low-temperature viscosities and VI values greater than 100 together with good solvency for additives. Other alkylated, multi-ring aromatic compounds may also be suitable as lubricant components for this invention, such as for example alkylated naphthalene. An example of such an alkyl naphthalene may be further described as having a mono alkyl substituent group of about 10 to about 20 carbon atoms having a kinematic viscosity at 100°C of about 2 cSt to about 8 cSt. Other alkylated aromatics which may be used when desirable are described, for example, in *"Synthetic Lubricants and High Performance Functional Fluids"*, Dressler, H., chap 5, (R. L. Shubkin (Ed.)), Marcel Dekker, N.Y. 1993.

Esters which may be useful as lubricant basestocks may contain mono-, di-, tri-, or tetra-carboxylate functionality. Such esters basestocks may include esters of dibasic acids with monoalkanols and the polyol esters of monocarboxylic acids. Esters of the former type include, for example, the esters of dicarboxylic acids such as phthalic acid, succinic acid, alkyl succinic acid, alkenyl succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acid, alkenyl malonic acid, etc., with a variety of alcohols such as butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, etc. Specific examples of these types of esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, etc.

Particularly useful synthetic esters are those which are obtained by reacting one or more polyhydric alcohols, preferably the hindered polyols such as the neopentyl polyols, e.g. neopentyl glycol, trimethylol ethane, 2-methyl-2-propyl-1,3-propanediol, trimethylol propane, pentaerythritol and dipentaerythritol; with alkanolic acids containing at least 4 carbon atoms, normally the C<sub>5</sub> to C<sub>30</sub> acids, such as the saturated straight chain fatty acids including caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, and behenic acid, or the corresponding branched chain fatty acids or the unsaturated fatty acids such as oleic acid.

Other suitable synthetic ester components are the esters of trimethylol ethane, trimethylol propane, trimethylol butane, pentaerythritol and/or dipentaerythritol with one or more monocarboxylic acids containing from about 5 to about 10 carbon atoms, which are widely available commercially.

The ester components typically have a kinematic viscosity at 100°C of about 2 cSt to about 20 cSt, more preferably about 2 cSt to about 8 cSt.

The optional basestock component of the present invention will typically be from about 0 to about 50 wt% of the total lubricant composition (all proportions and percentages set out in this specification are by weight unless the contrary is stated) and more usually in the range of about 5 to about 20 wt%.

#### VISCOSITY MODIFIER POLYMER (POLYMERIC THICKENER)

The lubricant compositions may also include a relatively high molecular weight component which has a marked viscosity thickening property when blended with the other components of the basestock. Such high molecular weight materials are generally polymeric materials, known alternatively as viscosity modifier polymers, polymeric thickeners, or viscosity index improvers. These polymeric components typically have a molecular weight from about 10,000 to 1,000,000, normally in the range of 100,000 to 1,000,000. Such polymeric components may include, for example, hydrogenated styrene-isoprene block copolymers, rubbers based on ethylene and propylene, high molecular weight acrylate or methacrylate esters, polyisobutylenes, and other materials of high molecular weight which are soluble in the basestocks and which, when added to the basestocks, confer the required viscosity to achieve the desired high-temperature viscosity grade *e.g.* 20, 30, 40, 50, 60, or higher.

In some instances, the formulated lubricants of this invention may not include viscosity modifier polymers. Using the wax isomerates described herein, narrowly crossgraded lubricants are achievable. For example, liquid lubricant compositions containing no viscosity modifier polymer may conform

to the SAE "xW-y" viscosity grading, where  $x = 0, 5, 10, \text{ or } 15$ , and where  $y = 10, 20, 30, \text{ or } 40$ , and where  $(y - x)$  is less than or equal to 25.

However, in many cases, viscosity modifier polymers in combination with lower viscosity basestocks have been found to be highly advantageous in achieving desired viscometric targets, particularly with multigrade lubricant oils. These polymer materials are readily available commercially from a number of suppliers according to type.

The preferred polymeric materials of this class for use in the present formulations are the block copolymers produced by the anionic polymerization of unsaturated monomers including styrene, butadiene, and isoprene. Copolymers of this type are described in U.S. Patents Nos. 5,187,236; 5,268,427; 5,276,100; 5,292,820; 5,352,743; 5,359,009; 5,376,722 and 5,399,629. Block copolymers may be linear or star type copolymers and for the present purposes, the linear block polymers are preferred. The preferred polymers are the isoprene-butadiene and isoprene-styrene anionic diblock and triblock copolymers. Particularly preferred high molecular weight polymeric components are the ones sold under the designation Shellvis™ 40, Shellvis™ 50 and Shellvis™ 90 by Shell Chemical Company, which are linear anionic copolymers. Of these, Shellvis™ 50, which is an anionic diblock copolymer, is preferred. A less preferred class of anionic block copolymers are the star copolymers such as Shellvis™ 200, Shellvis™ 260 and Shellvis™ 300. These high molecular weight solid materials, may conveniently be blended into lubricants in the form of a solution of the solid polymer in other basestock components. The amount of the high molecular weight thickener is typically from about 0.01 wt% to about 5 wt% of the total lubricant, more usually from about 0.1 wt% to about 3 wt% of the total lubricant composition, depending upon the viscosity of the basestock components and the desired viscometrics,

particularly with respect to the high-temperature grade requirements. For example, more widely cross-graded oils such as the 0W-40, 5W-50 and 10W-60 will normally require more of the high molecular weight polymer thickener than less widely cross-graded oils, for example 0W-20 and 10W-30 oils which will need little or none of this thickening material.

The types of high molecular weight polymers which may be used as thickeners or VI improvers is given by Klamann in *Lubricants and Related Products*, Verlag Chemie, Deerfield Beach, FL; ISBN 0-89573-177-0. Reference is also made to "*Lubricant Additives*" by M. W. Ranney, published by Noyes Data Corporation of Parkridge, N.J. (1973).

### PERFORMANCE ADDITIVES

The present lubricant compositions also include one or more performance additives to impart or enhance the desired performance properties of the finished oil. These additives and the overall package will generally be conventional in type. The types of additives which may normally be used include, for example, the following: (1) oxidation inhibitors, (2) dispersants, (3) detergents, (4) corrosion inhibitors, (5) metal deactivators, (6) anti-wear agents, (7) extreme pressure additives, (8) pour point depressants, (9) viscosity index improvers (VII), (10) seal compatibility agents, (11) friction modifiers, (12) defoamants, etc. These general component descriptions illustrate, but do not limit, the types and numbers of lubricant performance components which may be used in the formulated lubes of this invention.

Oxidative stability is provided by the use of antioxidants and for this purpose a wide range of commercially available materials is available, as noted by Klamann *op cit*. The most common types are the phenolic antioxidants and



the amine type antioxidants. They may be used individually by type or in combination with one another.

The phenolic antioxidants may be ashless (metal-free) phenolic compounds or neutral or basic metal salts of certain phenolic compounds. Typical phenolic antioxidant compounds are the hindered phenolics which are the ones which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Typical phenolic antioxidants include the hindered phenols substituted with  $C_6+$  alkyl groups and the alkylene coupled derivatives of these hindered phenols. Examples of phenolic materials of this type include: 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-di-t-butyl-4-heptyl phenol; and 2-methyl-6-di-t-butyl-4-dodecyl phenol. Examples of ortho coupled phenols include: 2,2'-bis(6-t-butyl-4-heptyl phenol); 2,2'-bis(6-t-butyl-4-octyl phenol); and 2,2'-bis(6-t-butyl-4-dodecyl phenol).

Non-phenolic oxidation inhibitors which may be used include the aromatic amine antioxidants and these may be used either as such or in combination with the phenolics. Typical examples of non-phenolic antioxidants include: alkylated and non-alkylated aromatic amines such as the aromatic monoamines of the formula  $R^3R^4R^5N$  where  $R^3$  is an aliphatic, aromatic or substituted aromatic group,  $R^4$  is an aromatic or a substituted aromatic group, and  $R^5$  is H, alkyl, aryl or  $R^6S(O)_xR^7$  where  $R^6$  is an alkylene, alkenylene, or aralkylene group,  $R^7$  is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group  $R^3$  may contain from 1 to about 20 carbon atoms, and preferably contains from 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both  $R^3$  and  $R^4$  are aromatic or substituted

aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups  $R^3$  and  $R^4$  may be joined together with other groups such as S.

Typical aromatic amine antioxidants have alkyl substituent groups of at least 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Polymeric amine antioxidants can also be used. Particular examples of aromatic amine antioxidants useful in the present invention include: p,p'-dioctyldiphenylamine; octylphenyl-beta-naphthylamine; t-octylphenyl-alpha-naphthylamine; phenyl-alphanaphthylamine; phenyl-beta-naphthylamine; p-octylphenyl-alpha-naphthylamine; 4-octylphenyl-l-octyl-beta-naphthylamine.

Normally, the total amount of antioxidants will not exceed 4 wt% of the total lubricant composition and normally is below about 3 wt%, typically from about 0.1 wt% to about 2 wt%.

Dispersants are also a known group of functional additives for lubricating oils, being used to maintain oxidation products in suspension in the oil, preventing accumulations of debris which could score bearings, block oilways and cause other types of damage as well as preventing deposit formation and inhibiting corrosive wear by the neutralization of acidic combustion products. Dispersants may be ash-containing or ashless in character. Chemically, many dispersants may be characterized as phenates, sulfonates, sulfurized phenates, salicylates, naphthenates, stearates, carbamates, thiocarbamates, and/or phosphorus deriva-

tives. A particularly useful class of dispersants are the alkenylsuccinic derivatives, typically produced by the reaction of a long chain substituted alkenyl succinic compound, usually a substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain group constituting the oleophilic portion of the molecule which confers solubility in the oil, is often a polyisobutylene group. Many examples of this type of dispersant are well known commercially and in the literature. Exemplary U.S. patents describing such disperants are 3,172,892; 3,2145,707; 3,219,666; 3,316,177; 3,341,542; 3,444,170; 3,454,607; 3,541,012; 3,630,904; 3,632,511; 3,787,374 and 4,234,435. Other types of dispersant are described in U.S. Patents Nos. 3,036,003; 3,200,107; 3,254,025; 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,413,347; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 4,454,059; 3,329,658; 3,449,250; 3,519,565; 3,666,730; 3,687,849; 3,702,300; 4,100,082; 5,705,458. A further description of dispersants may be found, for example, in EP 471 071, to which reference is made for this purpose.

Detergents are also important additive components, serving to maintain overall cleanliness. Chemically, many detergents are similar to the dispersants as noted by Klamann and Ranney *op cit*. Ranney discloses a number of overbased metal salts of various sulfonic acids which are useful as detergents/dispersants in lubricants. The book entitled "*Lubricant Additives*," C. V. Smallheer and R. K. Smith, published by the Lezius-Hiles Co. of Cleveland, Ohio (1967), similarly discloses a number of overbased sulfonates which are useful as dispersants/detergents, and such disclosure is incorporated herein by reference. Examples of detergents may include, without limitation, the ashless or metal containing salts of phenates, sulfonates, sulfurized phenates, salicylates, naphthenates, stearates, carbamates, thiocarbamates, and/or phosphorus derivatives.

Corrosion inhibitors or metal deactivators are not normally required in the present compositions but may be optionally added, depending on the type of metals to be encountered in operation. A wide variety of these are commercially available and are referred to also in Klamann, *op. cit.*

The antiwear agents and extreme pressure additives may be ash-containing or ashless in character. For example, certain ash-containing antiwear agents, typified by zinc dialkyl dithiophosphates such as zinc di(iso-hexyl) dithiophosphate, may be added as needed to the present lubricant compositions. Similarly, extreme pressure additives, exemplified by various sulfur-containing materials such as dimercaptothiadiazole, may also be used in the present lube formulations. The additional wear protection effect of such additives is desirable in preserving the engineering integrity of mechanical components operating under severe service conditions of high temperature and high load.

Pour point depressants, generally polymer-type materials, may be added as desired. These types of additives are described in Klamann, *op cit.* However, the wax isomerate basestocks described herein have a significant advantage in having sufficiently low pour points that added pour point depressants are not usually required. Thus, the low-pour wax isomerate basestocks offer an unexpected formulation advantage in simplyfying a performance additive system, and in avoiding potentially antagonistic interactions and incompatibilities among the several polymeric additives, such as dispersants and viscosity modifier polymers, that might be used in combination.

Seal compatibility agents may be required as the highly paraffinic nature of the primary basestocks generally makes it necessary to use this additive to meet seal compatibility specifications. Additives of this type are commercially available, for example, as various aromatic esters, and may be used in conven-

tional amounts, typically from about 0.1 to about 5 wt% of the total lubricant, usually from about 0.5 to about 2 wt%, depending on the particular basestock composition.

The friction modifiers (friction reducing agents) are a desirable class of additives and again, are commercially available as various fatty acid and/or ester derivatives. They also are described in Klamann, *op cit.* Glycerol esters such as the glycerol mono-oleates are often a preferred class of friction modifiers for the present lubricants; they are suitably used in an amounts from about 0.01 to about 2 wt% of the total lubricant. Alternate types of friction modifiers which may be used in the formulations of this invention are metal-containing friction modifiers, for example various molybdenum salts or complexes with functional groups such as dithiophosphates, dithiocarbamates, alcohols, amines, esters, and amides. Boron-containing friction modifiers with a similar array of functional groups, as cited above, may also be successfully used in such lubricant formulations. Effective amounts of metal-containing friction modifier additives may range from about 0.01 wt% to about 2 wt%.

Defoamants, typically silicone compounds, are commercially available and may be used in conventional minor amounts. Similarly, minor amounts of demulsifiers, for example oligomeric/polymeric ether-containing compounds, may also be used. Treat rates for these two types of additives (individually or combined) are typically less than about 1 percent and often less than about 0.1 percent.

## WAX ISOMERATE COMPOSITION AND PHYSICAL PROPERTIES

### Examples

In the following examples regarding wax isomerate lube basestocks, hydroisomerization and catalytic dewaxing reaction conditions were varied to obtain the desired products, with typical conditions ranging from, but not limited to, 200-370°C, 400-2000 psig, 0.50-2.0 hr<sup>-1</sup> LHSV, and 1900-5000 scf/B (standard cubic feet per barrel) H<sub>2</sub> at the reactor inlet.

### Examples 1-4

A hydrogenated Fischer-Tropsch wax (Paraflint 80) was hydrodewaxed in the presence of hydrogen over a combination of Pt/zeolite Beta hydroisomerization catalyst and Pt/ZSM-23 selective dewaxing catalyst. Four different hydrocarbon fluids were obtained under increasingly severe processing conditions, having KV (kinematic viscosity), VI (viscosity index) and PP (pour point) values as indicated in Table 3. Example 4 is an example of the primary basestock component of the present invention (Table 3).

### Examples 5 and 6

A hydrogenated and partially isomerized Middle Distillate Synthesis Waxy Raffinate (Shell MDS or "SMDS") was hydrodewaxed in the presence of hydrogen over the combination of catalysts used in Examples 1-4. Two different hydrocarbon fluids were obtained under increasingly severe processing conditions, having KV, VI and PP values as indicated in Table 3. Example 6 is an example of the primary basestock component of the present invention.

### Examples 7-9

The Shell MDS feedstock of Examples 5 and 6 was hydrodewaxed over synthetic ferrierite in the presence of hydrogen, under varying severity conditions to produce three different hydrocarbon fluids, having KV, VI and PP values as indicated in Table 3. Examples 7-9 are all examples of the primary basestock component of the present invention.

### Example 10

The waxy feedstock used in Examples 1-4 was hydrodewaxed over Pt/ZSM-48 in the presence of hydrogen to produce a hydrocarbon fluid having the KV, VI and PP values indicated in Table 3. Example 10 is an example of the primary basestock component of the present invention.

### Comparative Examples 1, 2, and 6

Commercially prepared polyalphaolefin basestocks of 3.87 cSt and 5.51 cSt KV at 100°C are characterized by pour points of <-65°C and VI's of 130 (Comparative Example 1) and 135 (Comparative Example 2), respectively. A commercial, higher viscosity grade of polyalphaolefin, 150 cSt KV at 100°C, is also included (Comparative Example 6). See Table 3.

### Comparative Examples 3-5

Several commercially prepared basestocks derived from hydrocracked crude oil fractions were also evaluated (Table 3). These included: a -18°C pour point, 5.1 cSt KV@100°C, 147 VI Shell XHVI basestock derived from hydro-isomerization of slackwax (Comparative Example 3); a 4.0 cSt KV@100°C, 114 VI Yukong 100N basestock, characterized by a pour point of -15°C (Compara-

tive Example 4); and a 6.9 cSt KV@100°C, 102 VI Chevron RLOP 240N basestock, also characterized by a pour point of -15°C (Comparative Example 5).

#### Comparative Example 7

Based on the art described in EP 0776959 A2, C80 Fischer-Tropsch wax feedstock was hydroisomerized at 399°C over Ni4352 catalyst, at 2000 psig, 1.28 hr<sup>-1</sup> LHSV (i.e., 1.00 kg/L/hr), and 6600 scf/B (i.e., 1500 NI/kg) H<sub>2</sub> at the reactor inlet, followed by distillation and solvent dewaxing of the 390°C+ fraction to give overall 48% yield of a lubricant basestock with the following properties: -17°C pour point, 5.68 cSt KV@100°C, 156 VI (Table 3). The Ni4352 catalyst is Ni/W on a fluorinated alumina support containing 8 wt% NiO, 24 wt% WO<sub>6</sub>, 3 wt% F, 1 wt% SiO<sub>2</sub> and 64 wt% Al<sub>2</sub>O<sub>3</sub>. Compositional analysis of the resulting fluid gave the following branching characteristics: branching index (BI) of 24.8, and branching proximity (CH<sub>2</sub>>4) of 25.1. Comparative example 7 falls outside the compositional space defined by equations (a) and (b) above for the primary wax isomerate basestocks described in the present invention.

Typical physical properties of various commercial lube basestocks are compared with those of the ULPP (ultra-low pour point) FT (Fischer-Tropsch) wax isomerates in Table 3, below.



TABLE 3. BASESTOCK PROPERTIES

<u>Description</u>	<u>Kinematic Viscosity</u> <u>@ 100°C (cSt)</u>	<u>Viscosity</u> <u>Index</u>	<u>Pour Point</u> <u>(°C)</u>
<b>Paraflint C80 Wax (Feed)</b>	9.42	-	83
Ex. 1	7.14	177	12
Ex. 2	6.52	171	-3
Ex. 3	5.72	161	-24
Ex. 4*	5.54	145	-63
<b>SMDS Waxy Raffinate (Feed)</b>	5.07	-	39
Ex. 5	5.23	142	-24
Ex. 6*	5.11	130	-66
Ex. 7*	5.33	149	-18
Ex. 8*	5.23	136	-59
Ex. 9*	5.46	144	-40
Ex. 10*	7.90	157	-42
<b>Comparative Examples</b>			
C.E. 1	3.87	130	<-65
C.E. 2	5.51	135	<-65
C.E. 3	5.06	147	-18
C.E. 4	4.00	114	-15
C.E. 5	6.94	102	-15
C.E. 6	150	214	-42
C.E. 7	5.68	156	-17

\* Examples of the primary basestock component of the present invention

Figure 1 is a comparison of the Cold Crank Simulation (CCS) performances of a typical hydroprocessed hydrocarbon lube basestock (XHVI) and two basestocks according to the present invention. CCS testing was conducted according to ASTM method D5392, which is used to measure the apparent viscosity of motor oils. The CCS viscometer measures the dynamic viscosity of fluids at low temperature and at high shear rate and stress, thus simulating the resistance to flow of oil in an engine crankcase at low temperature under starting (cranking) conditions. The data of Figure 1 demonstrates that the lubricant basestocks of the present invention have superior low temperature viscometric properties.

### Measurement of Branching Characteristics

#### Branching Index (BI)

For each basestock indicated in Table 3, 359.88 MHz  $^1\text{H}$  solution NMR spectra were obtained on a Bruker 360 MHz AMX spectrometer using 10% solutions in  $\text{CDCl}_3$ . TMS was the internal chemical shift reference.  $\text{CDCl}_3$  solvent gives a peak located at 7.28 ppm. All spectra were obtained under quantitative conditions using 90 degree pulse ( $10.9\mu\text{s}$ ), a pulse delay time of 30 s, which is at least five times the longest hydrogen spin-lattice relaxation time ( $T_1$ ), and 120 scans to ensure good signal-to-noise ratios.

H atom types were defined according to the following regions:

- 9.2-6.2 ppm hydrogens on aromatic rings;
- 6.2-4.0 ppm hydrogens on olefinic carbon atoms;
- 4.0-2.1 ppm benzylic hydrogens at the  $\alpha$ -position to aromatic rings;
- 2.1-1.4 ppm paraffinic CH methine hydrogens;
- 1.4-1.05 ppm paraffinic  $\text{CH}_2$  methylene hydrogens;
- 1.05-0.5 ppm paraffinic  $\text{CH}_3$  methyl hydrogens.

The branching index (BI) was calculated as the ratio in percent of non-benzylic methyl hydrogens in the range of 0.5 to 1.05 ppm, to the total non-benzylic aliphatic hydrogens in the range of 0.5 to 2.1 ppm. Results from these  $^1\text{H}$  NMR analyses are summarized in Table 4 below.

TABLE 4. % Different Types of H from  $^1\text{H}$  NMR

Description	% $\text{CH}_3$	% $\text{CH}_2$	% $\text{CH}$	BI
<u>Paraflint C80 Wax (Feed)</u>				
Ex. 1	19.4	78.5	2.1	19.4
Ex. 2	22.3	76.0	1.7	22.3
Ex. 3	25.6	71.8	2.6	25.6
Ex. 4*	27.6	68.1	4.3	27.6
<u>SMDS Waxy Raffinate (Feed)</u>	10.3	89.7	0.0	10.3
Ex. 5	23.6	70.1	6.3	23.6
Ex. 6*	29.8	67.8	2.4	29.8
Ex. 7*	26.2	71.2	2.6	26.2
Ex. 8*	30.0	67.0	3.0	30.0
Ex. 9*	27.9	69.9	2.2	27.9
Ex. 10*	27.0	70.8	2.2	27.0
<u>Comparative Examples</u>				
C.E. 1	22.7	74.8	2.5	22.7
C.E. 2	23.4	74.3	2.3	23.4
C.E. 3	26.9	69.4	3.7	26.9
C.E. 4	30.0	61.9	8.1	30.0
C.E. 5	31.5	55.3	13.2	31.5
C.E. 6	19.4	78.7	1.9	19.4
C.E. 7	24.8	73.5	1.7	24.8

\*Examples of the primary basestock component of the present invention

#### Branching Proximity ( $\text{CH}_2 > 4$ )

For each basestock indicated in Table 3, 90.5 MHz  $^{13}\text{C}$  NMR single pulse and 135 Distortionless Enhancement by Polarization Transfer (DEPT) NMR spectra were obtained on a Bruker 360 MHz AMX spectrometer using 10% solutions in  $\text{CDCl}_3$ . TMS was the internal chemical shift reference.  $\text{CDCl}_3$  solvent gives a triplet located at 77.23 ppm in the  $^{13}\text{C}$  spectrum. All single pulse spectra were obtained under quantitative conditions using 45 degree pulses (6.3  $\mu\text{s}$ ), a pulse delay time of 60 s, which is at least five times the longest carbon spin-lattice relaxation time ( $T_1$ ), to ensure complete relaxation of the sample, 200 scans to ensure good signal-to-noise ratios, and WALTZ-16 proton decoupling.

The C atom types CH<sub>3</sub>, CH<sub>2</sub>, and CH were identified from the 135 DEPT <sup>13</sup>C NMR experiment. A major CH<sub>2</sub> resonance in all <sup>13</sup>C NMR spectra at ~29.8 ppm is due to equivalent recurring methylene carbons which are four or more removed from an end group or branch; the percentage of such methylene carbons relative to all carbon types is the branching proximity, CH<sub>2</sub>>4. The types of branches were determined based primarily on the <sup>13</sup>C chemical shifts for the methyl carbon at the end of the branch or the methylene carbon one removed from the methyl on the branch. The proximity of branches, as indicated by CH<sub>2</sub>>4, and the type of carbons are summarized in Table 5.

TABLE 5. % Different Types of C from <sup>13</sup>C NMR

Description	%CH <sub>3</sub>	%CH <sub>2</sub>	%CH	CH <sub>2</sub> >4
<u>Parafint C80 Wax (Feed)</u>				
Ex. 1	13.6	81.3	5.1	38.2
Ex. 2	15.7	78.6	5.7	28.8
Ex. 3	17.3	76.3	6.3	22.5
Ex. 4*	18.0	75.5	6.5	14.7
<u>SMDS Waxy Raffinate (Feed)</u>	6.2	93.8	0	58.8
Ex. 5	16.6	77.3	6.0	17.3
Ex. 6*	24.9	67.4	7.7	7.7
Ex. 7*	16.4	77.5	6.1	21.8
Ex. 8*	19.3	75.1	5.6	12.8
Ex. 9*	18.1	76.3	5.6	17.7
Ex. 10*	15.9	76.3	7.7	20.5
<u>Comparative Examples</u>				
C.E. 1	11.4	83.7	4.9	20.4
C.E. 2	13.2	81.0	5.8	20.6
C.E. 3	19.0	74.3	6.7	22.6
C.E. 4	16.7	72.3	11.0	20.4
C.E. 5	16.5	72.0	21.5	19.2
C.E. 6	12.3	83.9	3.8	17.3
C.E. 7	15.9	79.3	4.8	25.1

\* Examples of the primary basestock component of the present invention

The branching characteristics and pour points of the isoparaffinic components of the exemplary basestocks, as disclosed in Tables 3-5, are compared in the following Table 6.

TABLE 6. Comparison of Isoparaffinic Lube Compositions

<u>Description</u>	<u>BI</u>	<u>CH<sub>2</sub>&gt;4</u>	<u>Pour Point, °C</u>
<u>Paraflint C80 Wax (Feed)</u>			83
Ex. 1	19.4	38.2	12
Ex. 2	22.3	28.8	-3
Ex. 3	25.6	22.5	-24
Ex. 4*	27.6	14.7	-63
<u>SMDS Waxy Raffinate (Feed)</u>	10.3	58.8	39
Ex. 5	23.6	17.3	-24
Ex. 6*	29.8	7.7	-66
Ex. 7*	26.2	21.8	-18
Ex. 8*	30.0	12.8	-59
Ex. 9*	27.9	17.7	-40
Ex. 10*	27.0	20.5	-42
<u>Comparative Examples</u>			
C.E. 1	22.7	20.4	<-65
C.E. 2	23.4	20.6	<-65
C.E. 3	26.9	22.6	-18
C.E. 4	30.0	20.4	-15
C.E. 5	31.5	19.2	-15
C.E. 6	19.4	17.3	-42
C.E. 7	24.8	25.1	-17

\* Examples of the primary basestock component of the present invention

The primary basestocks of the present invention can be differentiated from other hydrocarbon basestocks by the extent of branching as indicated by BI and the Branching Proximity as indicated by CH<sub>2</sub>>4. These compositional fingerprints are graphed to aid in defining unique regions in this 2-dimensional composition space as illustrated in Figure 2 (left quadrant).

From Figure 2 it is clear that the branching characteristics of the primary isoparaffinic basestock compositions of the present invention are within a unique

region. Specifically, the composition can be described as comprising mixtures of paraffinic hydrocarbon components in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more removed from an end group or branch ( $\text{CH}_2>4$ ), are such that:

- (a)  $\text{BI} - 0.5 (\text{CH}_2>4) > 15$ ; and
- (b)  $\text{BI} + 0.85 (\text{CH}_2>4) < 45$ .

Figure 3 is a comparison of the dynamic viscosities ( $\text{DV}@-40^\circ\text{C}$ ), measured by the CCS method, and the kinematic viscosities ( $\text{KV}@100^\circ\text{C}$ ) of various hydrocarbon fluids, including the primary basestock components of the present invention. The fluids of the present invention are indicated as "FTWT" (Fischer Tropsch Wax Isomerate), while several conventional hydrocracked stocks are indicated as "HDC." In particular, the HDC data points representing Comparative Examples 3-5 of the present specification are included. These viscosity data are listed in Table 7.

TABLE 7.  
High- and Low-Temperature Viscosity Relationship:  
Wax Isomerate vs Hydrocracked.

<u>Basestock</u> <u>Type</u>	<u>Pour</u>	<u>KV100</u> <u>(cSt)</u>	<u>CCS</u>	<u>BI</u>	<u>CH<sub>2</sub>&gt;4</u>	<u>Within WI</u>
	<u>Point</u> <u>(°C)</u>		<u>Viscosity</u> <u>@</u> <u>-40°C (cP)</u>			<u>Lube</u> <u>Composition</u> <u>Space?</u>
FTWI	-34	3.83	1940	29.9	16.8	Yes
FTWI	-34	4.02	2520	29.9	16.1	Yes
FTWI	-59	5.23	7770	30.0	12.8	Yes
FTWI	-18	5.33	7290	26.2	21.8	Yes
FTWI	-40	5.46	4500	27.9	17.7	Yes
FTWI	-26	6.00	6630	26.9	19.2	Yes
FTWI	-37	6.03	7360	28.2	17.9	Yes
FTWI	-42	7.95	14960	27.0	20.5	Yes
HDC	-18	5.06	11190	26.9	22.6	No
HDC	-15	4.00	6400	30.0	20.4	No
HDC	-15	6.94	>23000	31.5	19.2	No
HDC	-14	4.03	12700	31.5	15.9	No

It is clear from the data set forth in Figure 3 that the FTWI fluids of the present invention have significantly improved low-temperature viscosity characteristics compared to that of conventional HDC fluids of the prior art. The solid line fits the viscosity trend of the FTWI basestocks of this invention, and the dotted line (parallel to the FTWI trend line) defines a boundary between the dynamic viscosity of the HDC oils and that of the FTWI oils. Note that all of the primary liquid hydrocarbon fluids of the present invention fall below the dotted line on the graph and can therefore be described by the following equation for dynamic viscosity (DV):

$$(c) \quad DV_{@-40^{\circ}\text{C}} < 2900(KV_{@100^{\circ}\text{C}}) - 7000.$$

## WAX ISOMERATE BASESTOCK PERFORMANCE

### Composition and Properties

Additional wax isomerate basestocks were used in discovering the unexpected performance advantages in formulated lubricants. Process conditions for hydroisomerization and catalytic dewaxing reactions for converting waxy feed stock into wax isomerate basestock are described above. These basestocks are listed in Table 8. All wax isomerates designated A, B, or C are examples of the primary basestock components of the present invention, and fall within the compositional space defined above, equations (a) and (b), using BI and  $\text{CH}_2 > 4$  parameters. For comparison, conventional hydroprocessed basestocks Shell XHVI and Chevron UCBO (D-1, D-2), a high-pour point wax isomerate (D-3), and synthetic PAO4 (E-1) are listed, and fall outside of the basestock compositional space defined by equations (a) and (b).



TABLE 8. Lubricant Basestocks Composition and Physical Properties

<u>Basestocks</u> *	<u>Basestock</u> <u>Type</u>	<u>Pour</u> <u>Point</u> (°C)	<u>KV100</u> (cSt)	<u>Viscosity</u> <u>Index</u>	<u>BI</u>	<u>CH<sub>2</sub>&gt;4</u>	<u>Within</u> <u>WI Lube</u> <u>Composition</u> <u>Space?</u>
A-1	Wax	-66	3.7	122	33.0	9.4	Yes
	Isomerate						
A-2	Wax	-49	4.1	135	30.8	13.3	Yes
	Isomerate						
A-3	Wax	-60	6.0	139	30.3	10.5	Yes
	Isomerate						
A-4	Wax	-57	8.5	143	28.8	13.7	Yes
	Isomerate						
A-5	Wax	-51	12.2	145	27.0	16.1	Yes
	Isomerate						
B-1	Wax	-34	4.0	141	29.9	16.1	Yes
	Isomerate						
B-2	Wax	-40	4.1	139	29.9	13.7	Yes
	Isomerate						
B-3	Wax	-37	6.0	154	28.2	17.9	Yes
	Isomerate						
B-4	Wax	-39	8.0	157	27.0	20.5	Yes
	Isomerate						
C-1	Wax	-20	3.7	148	27.5	19.0	Yes
	Isomerate						
C-2	Wax	-26	6.0	156	26.9	19.2	Yes
	Isomerate						
D-1	Chevron UCBO	-20	4.2	130	28.2	20.6	No
D-2	Shell XHVI	-18	4.0	143	25.8	24.7	No
D-3	Wax	-18	6.0	164	25.4	21.5	No
	Isomerate						
E-1	PAO4	-71	4.0	125	21.1	20.3	No

**\*Comments:**

"A" represents WI oils with nominal pour points lower than about -45°C

"B" represents WI oils with nominal pour points in the range of about -30°C to -45°C

"C" represents WI oils with nominal pour points higher than about -30°C

### BASESTOCK BIODEGRADATION CHARACTERISTICS

The OECD and CEC biodegradation of various wax-isomerate basestocks and other types of basestocks were tested and results are tabulated in the following Table 9.

TABLE 9. Lubricant Basestock Biodegradability

<u>Basestocks</u>	<u>Basestock Type</u>	<u>Pour Point (°C)</u>	<u>KV100 (cSt)</u>	<u>% Biodegradability</u>	
				<u>OECD 301B @ 28 days</u>	<u>CEC L-33-A-93 @ 21 days</u>
A-1	Wax Isomerate	-66	3.7	54	74
A-2	Wax Isomerate	-49	4.1	61	90
A-3	Wax Isomerate	-60	6.0	55	51
B-1	Wax Isomerate	-34	4.0	65	98
B-2	Wax Isomerate	-40	4.1	65	90
B-3	Wax Isomerate	-37	6.0	67	90
C-1	Wax Isomerate	-20	3.7	72	100
D-1	RLOP UCBO	-20	4.2	34	82
D-2	Shell XHVI	-18	4.0	50	89
E-1	PAO4	-71	4.0	30	37

In the very demanding OECD 301B test, the wax isomerates of the current invention attain greater than about 50% biodegradation.

### BASESTOCK PERFORMANCE CHARACTERISTICS

In the lubricant formulations defined in this invention, the wax isomerate basestocks described herein meet the compositions defined by equations (a) and (b), and additionally fall into preferred ranges of certain performance parameters such as pour point, MRV viscosity, and viscosity index. A series of WI basestocks of the present invention with differing pour points but with matching kinematic viscosity (6.0 cSt) at 100°C are listed in Table 10. Other basestock

performance properties include Viscosity Index, MRV viscosity, and CCS viscosity.

**TABLE 10. Wax Isomerate Performance Properties vs Pour Point**

<u>Basestock</u>	<u>Basestock Type</u>	<u>Pour Point (°C)</u>	<u>KV100 (cSt)</u>	<u>Viscosity Index</u>	<u>MRV Viscosity @-30°C (cP); Yield Stress &lt;35 Pa</u>	<u>CCS Viscosity @ -30°C (cP)</u>
A-3	Wax	-60	5.97	139	3060	3060
	Isomerate					
B-3	Wax	-37	6.03	154	2730	2350
	Isomerate					
C-2	Wax	-26	6.00	156	3050	2240
	Isomerate					
D-3	Wax	-18	6.02	164	9210	2110
	Isomerate					

Figure 4 is a comparison of the data presented in Table 10, including viscosity index (VI), mini-rotary viscometer (MRV) viscosity, and cold crank simulation (CCS) viscosity.

MRV testing was conducted according to ASTM method D4684. MRV testing is conducted by very slowly cooling down a lube with the resulting slow crystallization of the wax contained in the lube, followed by testing the wax matrix strength and lube viscosity under low energy, low shear conditions. Thus MRV measures the dynamic viscosity of a fluid at low temperature and at low shear rate and stress, under simulated pumping conditions.

CCS testing was conducted according to ASTM method D5392, which is used to measure the apparent viscosity of motor oils at low temperatures. CCS testing is conducted by rapidly cooling down a lube with resulting rapid precipitation of wax contained in the lube, followed by measuring the resistance to flow of the waxy lubricant under high energy, high shear conditions. Thus

CCS measures the dynamic viscosity of fluids at low temperature and at high shear rate and stress, under conditions simulating engine starting (mechanical cranking).

The viscosity index (VI) is a measure of a fluid's retention of viscosity with increasing temperature; thus high VI fluids retain greater viscosity and do not thin out as quickly as low VI fluids do with increasing temperature.

The data of Figure 4 demonstrates that the primary wax isomerate basestocks of the present invention should have pour points of about -25°C or lower, at which point the combination of MRV viscosity and CCS viscosity (both measured at -30°C) is lowest. Such a combination of these two low-temperature performance properties is highly advantageous in preparing fully-formulated wax isomerate-containing lubricants, and was not predictable based on the WI basestock compositions defined by equations (a) and (b). In addition, an upper limit to VI is realized, preferably at about 160.

### Lubricant Formulations

In the following examples regarding formulations and finished lube performance properties, various passenger car engine oils (PCEO) are illustrated, using an additive package (PCEO DDI) having the proven capability of meeting the quality standards defined by API SJ (ASTM 4485; API Publication No. 1509, Appendix G), ILSAC GF2 (API Publication No. 1509, Appendix D), and ACEA A3/B3 (ACEA European Oil Sequences, Sept. 1999, [www.acea.be](http://www.acea.be)). The PCEO DDI additive package contains the following performance additives (typically used in engine oil formulations): dispersants, detergents, antiwears, antioxidants, seal compatibility additives, friction modifiers, and demulsifier/defoamants. The basestock mixture is also typical of high-quality

PCEO's, specifically semi-synthetic or fully synthetic engine oils where a major amount of one or more highly paraffinic hydrocarbons (e.g., in this invention, WI basestocks) is used, in addition to optional minor amounts of one or more co-basestocks (e.g., esters, alkyl aromatics, etc.; to enhance as needed additive solubility, seal compatibility, or other basestock-related performance).

Formulated lubricants are prepared by combining all the basestock and additive components together, and heating the mixture to 70-90°C with stirring for several hours until all components are dissolved and the mixture is completely homogeneous. Details of the specific formulations used for each of the Examples and Comparative Examples are listed in the associated Tables.

Several wax isomerate lubricant compositions at selected kinematic viscosity at 100°C and at selected pour point (Table 8) were formulated with an API SJ-quality additive package (PCEO DDI) as well as additional lubricating components to obtain examples of multi-grade passenger car engine oils. Formulation examples are listed below.

#### Examples 11-14

These examples (Table 11) include non-viscosity modified (non-VM) oils formulated with ultra low pour point (A-1) and low pour point (B-2, B-3, B-4) wax isomerates as the major paraffinic basestock component, to give multigrade (0W-20, 5W-20, and 10W-30) lubricants.

#### Examples 15-20

These examples (Tables 12-14) include polymer-modified oils formulated with selected wax isomerate basestocks from both A and B categories (Table 8)

as the major paraffinic basestock component, to give various multigrade lubricants.

#### Comparative Examples 8, 11-13

These comparative examples (Tables 11, 13, 14) include polymer-modified oils formulated with PAO synthetic basestock as the major paraffinic basestock component, to give various multigrade lubricants.

#### Comparative Examples 9, 10

These comparative examples (Table 12) include polymer-modified oils formulated with conventional hydroprocessed basestocks Shell XHVI (D-1) and Chevron UCBO (D-2) as the major paraffinic basestock component, to give various multigrade lubricants.

Table 11 shows examples of non-viscosity modified multigrade PCEO's. WI basestocks of this invention demonstrate the unexpected capability of formulating naturally crossgraded oils, as demonstrated by Examples 11 (SAE 0W-20), 12 (SAE 0W-20), 13 (SAE 5W-20) and 14 (SAE 10W-30). Multigrade oils formulated without viscosity modifier polymers (so called non-viscosity modified, or non-VM oils) have been only achieved with polyalphaolefins, for example with hydrogenated poly-1-decene as cited in U.S. Patent No. 4,992,183. Compable non-VM formulations have not been obtainable with conventionally hydroprocessed basestocks.

**TABLE 11.**  
**Wax Isomerate Performance in Non-Viscosity Modified Formulations**

Formulation Component, Wt%	Example 11	Example 12	Example 13	Example 14	C.E. 8
Wax Isomerate A-1	64.1				
Wax Isomerate B-2		64.1			
Wax Isomerate B-3			64.1		
Wax Isomerate B-4				64.1	
Syn. Base Oil (PAO)					64.1
Co-Base Oil	20.0	20.0	20.0	20.0	20.0
(Ester/Aromatic)					
PCEO DDI (Additives)	15.9	15.9	15.9	15.9	15.9
<b>Performance</b>					
SAE Viscosity Grade	0W-20	0W-20	5W-20	10W-30	10W-30
KV @ 100°C (cSt)	6.25	6.60	8.60	10.45	10.49
CCS @ -20°C (cP)				2800	3220
CCS @ -25°C (cP)			3025		
CCS @ -30°C (cP)	2570	2490			
HTHS @ 150°C (cP)	2.14	2.35	2.96	3.44	3.42
Pour Point (°C)	-54	-51	-45	-51	-54
MRV @ -30°C (cP/Pa)				8830/<35	10600/<35
MRV @ -35°C (cP/Pa)			10100/<35		
MRV @ -40°C (cP/Pa)	9580/<35	8660/<35			

Table 12 lists examples which demonstrate that wax isomerate basestocks of this invention can meet the stringent viscosity requirements of low-viscosity multigraded oils, specifically SAE 0W-30, under formulation conditions where conventional hydroprocessed basestocks fail. Even though each example was prepared with an identical formulation, Example 15 successfully meets all viscometric targets for a 0W-30 multigrade oil, whereas Comparative Example 9 fails to meet the CCS viscosity requirement (3250 cP maximum at -30°C), and Comparative Example 10 fails to meet the MRV viscosity requirement at -40°C (60000 cP maximum, with yield stress <35 Pa).

TABLE 12.  
Wax Isomerate Performance in SAE Viscosity Grade 0W-30 Formulations

Formulation Component, Wt%	Ex. 15	C.E. 9	C.E. 10
Styrene-Isoprene Polymer	0.9	0.9	0.9
Wax Isomerate B-1	54.7		
Chevron UCBO, D-1		54.7	
Shell XHVI, D-2			54.7
Co-Base Oil (Ester/Aromatic/PAO)	28.5	28.5	28.5
PCEO DDI (Additives)	15.9	15.9	15.9
<u>Performance</u>			
SAE Viscosity Grade	0W-30	5W-30	15W-30
KV @100°C (cSt)	9.8	10.2	9.8
CCS @ -30°C (cP)	2850	3860*	3220
HTHS @ 150°C (cP)	3.16	3.34	3.20
Pour Point (°C)	-46	-31	-22
MRV @ -25°C (cP/Pa)			4800/<35
MRV @ -30°C (cP/Pa)			162000/<70
MRV @ -40°C (cP/Pa)	12500/<35	35600/<35	Too viscous to measure*

\*Fails to meet target requirements for SAE 0W-30

Table 13 lists formulated oils of this invention demonstrating utility of the WI basestocks described herein as formulation components in low-viscosity, widely crossgraded oils, such as for example SAE 0W-40. Examples 16 and 18, formulated with WI basestocks A-1 (-66°C pour point) and B-1 (-34°C pour point), successfully meet the viscometric targets of SAE 0W-40, comparing favorably with the fully synthetic Comparative Example 11. Such performance cannot be attained by comparably formulated lubricants using conventionally hydroprocessed basestocks.

Additionally, in certain formulations such as for example SAE 0W-40, preferred WI basestocks may have higher pour points because of more advantageous (i.e., lower) CCS viscosity compared to WI basestocks with ultra low pour points. Examples 17 and Example 18 compare the performance of lubricants formulated with WI isomerate basestocks with essentially identical



kinematic viscosity at 100°C, nominal 4 cSt, but differing in pour point, -49°C pour (A-2 basestock) versus -34°C pour (B-1 basestock), respectively. Example 18, containing the higher pour B-1, meets the target viscometrics for SAE 0W-40. By comparison Example 17, containing the lower pour A-1, fails to meet the low-temperature CCS viscosity target for SAE 0W-40 grade. Alternatively, very low pour point WI basestocks may be used in such cases, however, as in Example 16 using A-1 (3.7 cSt, and -66°C pour point), but the usable WI basestocks have lower kinematic viscosity at 100°C to compensate for its higher CCS viscosity. Lowering kinematic viscosity may balance CCS requirements, but could cause other potentially undesirable changes, such as for example increasing basestock volatility.

TABLE 13.

Wax Isomerate Performance in SAE Viscosity Grade 0W-40 Formulations

Formulation Component, Wt%	Example 16	Example 17	Example 18	Comp. Ex. 11
Styrene-Isoprene Polymer	1.4	1.4	1.4	1.6
Wax Isomerate A-1	62.7			
Wax Isomerate A-2		62.7		
Wax Isomerate B-1			62.7	
Syn. Base Oil (PAO)				62.5
Co-Base Oil (Ester/Aromatic)	20.0	20.0	20.0	20.0
PCEO DDI (Additives)	15.9	15.9	15.9	15.9
<u>Performance</u>				
SAE Viscosity Grade	0W-40	5W-40	0W-40	0W-40
KV @100°C (cSt)	12.7	13.5	13.5	14.1
CCS @ -30°C (cP)	3150	3340*	2800	3100
HTHS @ 150°C (cP)	3.54	3.75	3.70	3.72
Pour Point (°C)	-56	-51	-48	-60
MRV @ -40°C (cP/Pa)	18370/<35	20000/<35	16800/<35	18000/<35

\* Fails to meet target requirements for SAE 0W-40

Table 14 lists formulated oils demonstrating the use of WI isomerate basestocks in attaining alternate engine oil multigrades, such as for example

SAE 15W-50 and SAE 5W-50. Both A-type WI basestocks, as in Example 19, and B-type WI basestocks, as in Example 20, can be used in such formulations.

**TABLE 14.**  
**Wax Isomerate Performance in SAE**  
**Viscosity Grade 15W-50, 5W-50 Formulations**

Formulation Component, Wt%	Example 19	Example 20	C.E. 12	C.E. 13
Styrene-Isoprene Polymer	1.0	2.0	1.25	2.0
Wax Isomerate A-3	9.5			
Wax Isomerate A-4	36.4			
Wax Isomerate A-5	17.2			
Wax Isomerate B-2		43.1		
Wax Isomerate B-3		19.0		
Wax Isomerate B-4				
Syn. Base Oil (PAO)			62.85	62.1
Co-Base Oil (Ester/Aromatic)	20.0	20.0	20.0	20.0
PCEO DDI (Additives)	15.9	15.9	15.9	15.9
<b>Performance</b>				
SAE Viscosity Grade	15W50	5W-50	15W-50	5W-50
KV @100°C (cSt)	17.8	21.5	18.0	20.7
CCS @ -15°C (cP)	2660		2390	
CCS @ -25C (cP)		2580		2500
HTHS @ 150°C (cP)	4.97	4.90	5.05	4.74
Pour Point (°C)	-51	-48	-48	-54
MRV @ -25°C (cP/Pa)	11200/<35		10100/<35	
MRV @ -35°C (cP/Pa)		18300/<35		16500/<35

Table 15 demonstrates the advantageous biodegradability of a fully formulated wax isomerate lubricant versus a comparable fully formulated PAO lubricant. This confirms that the superior biodegradability of wax isomerate base oils relative to PAO base oil (Table 9) translates into a significant advantage in wax-isomerate containing formulated lubricants.

TABLE 15. Biodegradation of Wax Isomerate SAE 0W-40 Formulation

Formulation Component, wt%	Example 18	Comp. Ex. 11
Styrene-Isoprene Polymer	1.4	1.6
Wax Isomerate B-1	62.7	
Syn. Base Oil (PAO)		62.5
Co-Base Oil (Ester/Aromatic)	20.0	20.0
PCEO DDI (Additives)	15.9	15.9
<u>Performance</u>		
SAE Viscosity Grade	0W-40	0W-40
<u>% Biodegradability:</u>		
OECD 301B @ 28 days	53	21
CEC L-33-A-93 @ 21 days	71	45

Although the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the scope and spirit of the present invention.

## CLAIMS:

## 1. A liquid lubricant composition, comprising

(i) a paraffinic biodegradable hydrocarbon basestock component having a biodegradability of at least 50% (OECD 301B) and having a pour point of about -25°C or lower, in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ( $\text{CH}_2>4$ ), are such that:

$$(a) \quad \text{BI} - 0.5(\text{CH}_2>4) > 15; \text{ and}$$

$$(b) \quad \text{BI} + 0.85(\text{CH}_2>4) < 45;$$

as measured over said hydrocarbon basestock as a whole, and

(ii) additives soluble in the basestock comprising a detergent and an antioxidant, the liquid lubricant composition having a CCS viscosity at -15°C of not more than about 3500 cP and a kinematic viscosity at 100°C of not less than about 5 cSt.

2. The liquid lubricant composition of claim 1, wherein a combination of dynamic viscosity (DV), as measured by CCS viscosity at -40°C, and kinematic viscosity, as measured at 100°C, of said paraffinic biodegradable hydrocarbon basestock is:

$$\text{DV}_{@-40^\circ\text{C}} < 2900(\text{KV}_{@100^\circ\text{C}}) - 7000.$$

3. The liquid lubricant composition of claim 1, wherein MRV viscosity as measured at -30°C of said paraffinic biodegradable hydrocarbon basestock is not more than about 60,000 cP, with a yield stress of not more than about 35 cP.

4. The liquid lubricant composition of claim 3, wherein MRV viscosity as measured at -40°C of said paraffinic biodegradable hydrocarbon basestock is not more than about 60,000 cP, with a yield stress of not more than about 35 cP.

5. The liquid lubricant composition of claim 1, wherein viscosity index of said paraffinic biodegradable hydrocarbon basestock is about 160 or less.

6. The liquid lubricant composition of claim 5, wherein the viscosity index of said paraffinic biodegradable hydrocarbon basestock is from about 140 to about 160.

7. The liquid lubricant composition of claim 1, wherein the pour point of said paraffinic biodegradable hydrocarbon basestock is less than about -30°C.

8. The liquid lubricant composition of claim 7, wherein MRV viscosity as measured at -35°C of said paraffinic biodegradable hydrocarbon basestock is not more than about 60,000 cP, with a yield stress of not more than about 35 cP.

9. The liquid lubricant composition of claim 7, wherein viscosity index of said paraffinic biodegradable hydrocarbon basestock is from about 140 to about 160.

10. The liquid lubricant composition of claim 7, wherein the pour point of said paraffinic biodegradable hydrocarbon basestock is from about -30°C to about -45°C.

11. The liquid lubricant composition of claim 1, wherein the pour point of said lubricant composition is less than about -20°C.

12. The liquid lubricant composition of claim 11, wherein the pour point of said lubricant composition is less than about  $-30^{\circ}\text{C}$ .

13. The liquid lubricant composition of claim 11, wherein the pour point of said lubricant composition is from about  $-35^{\circ}\text{C}$  to about  $-60^{\circ}\text{C}$ .

14. The liquid lubricant composition of claim 1 which conforms to SAE 0W low-temperature viscosity grading, and which has CCS viscosity  $-30^{\circ}\text{C}$  of not more than 3250 cP, and MRV viscosity at  $-40^{\circ}\text{C}$  of not more than 60,000 cP.

15. The liquid lubricant composition of claim 14 further comprising a polymeric viscosity modifier.

16. The liquid lubricant composition of claim 15 which conforms to SAE 0W-40 grading and which has a kinematic viscosity at  $100^{\circ}\text{C}$  of from 12.5 cSt to less than 16.3 cSt, comprising from about 0.05 to 30 wt% of the polymeric viscosity modifier and wherein the paraffinic biodegradable hydrocarbon base-stock has a kinematic viscosity at  $100^{\circ}\text{C}$  of from about 3.5 cSt to about 5.0 cSt.

17. The liquid lubricant composition of claim 16 having a pour point no higher than about  $-40^{\circ}\text{C}$ .

18. The liquid lubricant composition of claim 15 which conforms to SAE 0W-30 grading and which has a kinematic viscosity at  $100^{\circ}\text{C}$  of from 9.3 cSt to less than 12.5 cSt, comprising from about 0.01 to about 25 wt% of the polymeric viscosity modifier and wherein the paraffinic biodegradable hydrocarbon basestock has a kinematic viscosity at  $100^{\circ}\text{C}$  of from about 3.5 to about 5.0 cSt.

19. The liquid lubricant composition of claim 18 having a pour point no higher than about  $-40^{\circ}\text{C}$ .

20. The liquid lubricant composition of claim 19 having a CCS viscosity at  $-30^{\circ}\text{C}$  of not more than about 3000 cP.

21. The liquid lubricant composition of claim 1 which conforms to SAE 5W low-temperature viscosity grading, and which has CCS viscosity at  $-25^{\circ}\text{C}$  of not more than 3500 cP, and MRV viscosity at  $-35^{\circ}\text{C}$  of not more than 60,000 cP.

22. The liquid lubricant composition of claim 21 further comprising a polymeric viscosity modifier.

23. The liquid lubricant composition of claim 1 which conforms to SAE 10W low-temperature viscosity grading, and which has CCS viscosity at  $-20^{\circ}\text{C}$  of not more than 3500 cP, and MRV viscosity at  $-30^{\circ}\text{C}$  of not more than 60,000 cP.

24. The liquid lubricant composition of claim 23 further comprising a polymeric viscosity modifier.

25. The liquid lubricant composition of claim 1 which conforms to SAE 15W low-temperature viscosity grading, and which has CCS viscosity at  $-15^{\circ}\text{C}$  of not more than 3500 cP, and MRV viscosity at  $-25^{\circ}\text{C}$  of not more than 60,000 cP.

26. The liquid lubricant composition of claim 25 further comprising a polymeric viscosity modifier.

27. The liquid lubricant composition of claim 26 which conforms to SAE 15W-50 viscosity grading and which has a kinematic viscosity at 100°C of from 16.3 cSt to less than 21.9 cSt, comprising from about 0.1 to about 25 wt% of the polymeric viscosity modifier and wherein the paraffinic biodegradable hydrocarbon basestock has a kinematic viscosity at 100°C of from about 5.5 cSt to about 14.0 cSt.
28. The liquid lubricant composition of claim 27 having a pour point no higher than about -35°C.
29. The liquid lubricant composition of claim 28 having a CCS viscosity at -30°C of not more than about 3300 cP.
30. The liquid lubricant composition of claim 1 which conforms to SAE "xW-y" viscosity grading, where x = 0, 5, 10, or 15, and where y = 10, 20, 30, or 40, and where (y - x) is less than or equal to 25.
31. The liquid lubricant composition of claim 1, wherein said paraffinic hydrocarbon components have BI greater than 26.1 and  $\text{CH}_2 > 4$  less than 22.2.
32. The liquid lubricant composition of claim 1 further comprising a lubricating oil basestock component comprising an ester or an alkylated aromatic or mixtures thereof.
33. The liquid lubricant composition of claim 32 wherein the ester is an ester of a polyol alcohol and a monocarboxylic acid having a kinematic viscosity at 100°C of about 2 cSt to about 8 cSt, and the alkylated aromatic is an alkyl naphthalene having a mono alkyl substituent group of about 10 to about 20



carbon atoms having a kinematic viscosity at 100°C of about 2 cSt to about 8 cSt.

34. The liquid lubricant composition of claim 32 having from about 5 wt% to about 20 wt% of the ester or alkylated aromatic or mixture thereof.

35. The liquid lubricant composition of claim 1 wherein the antioxidant is an aromatic amine or an alkylated phenol or mixtures thereof.

36. The liquid lubricant composition of claim 1 wherein the detergent is an alkali or alkaline earth sulfonate, or an alkali or alkaline earth salicylate, or alkali or alkaline earth phenate, or mixtures thereof.

# Low-Temperature CCS Viscosity Comparison

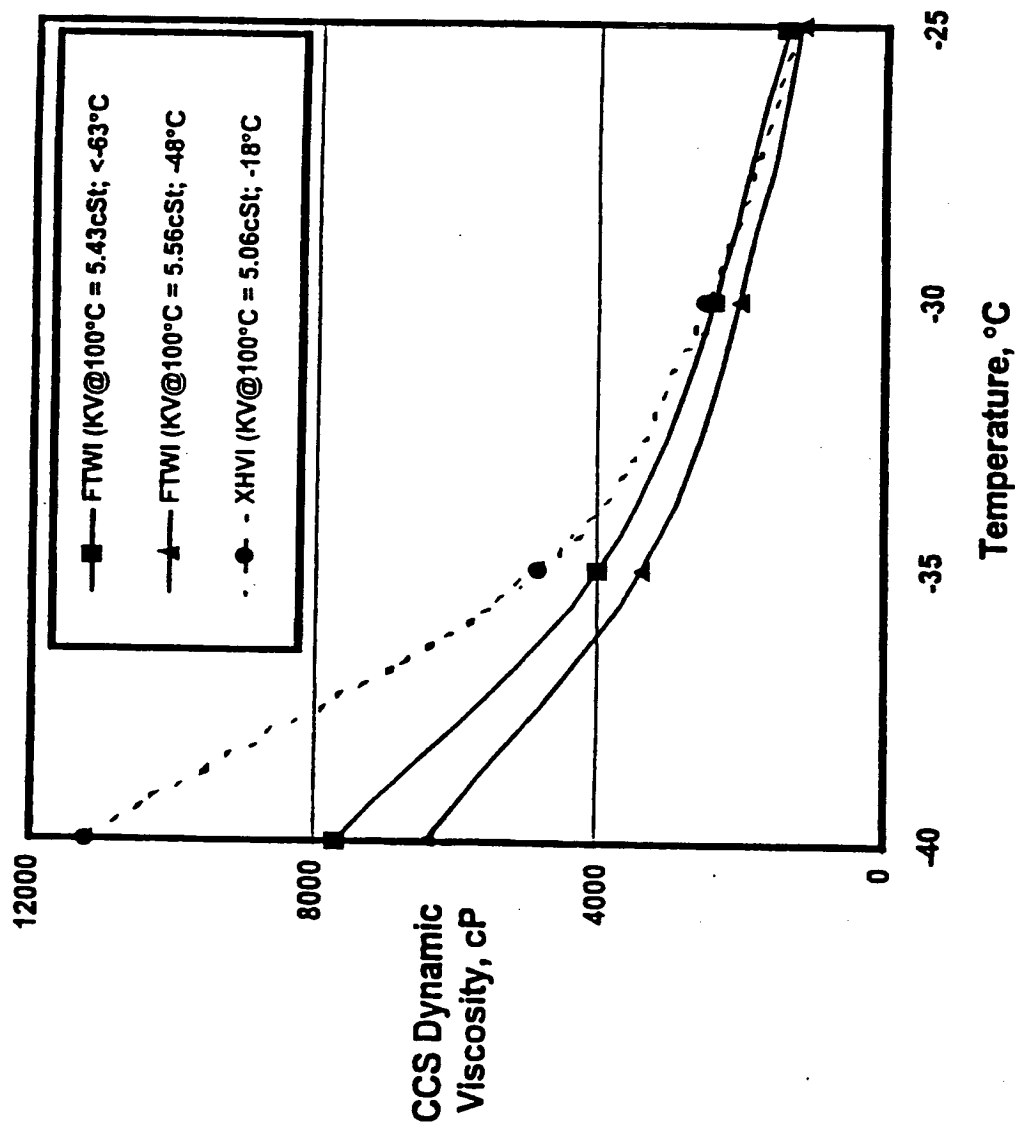


FIG. 1

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## Unique Lube Compositions

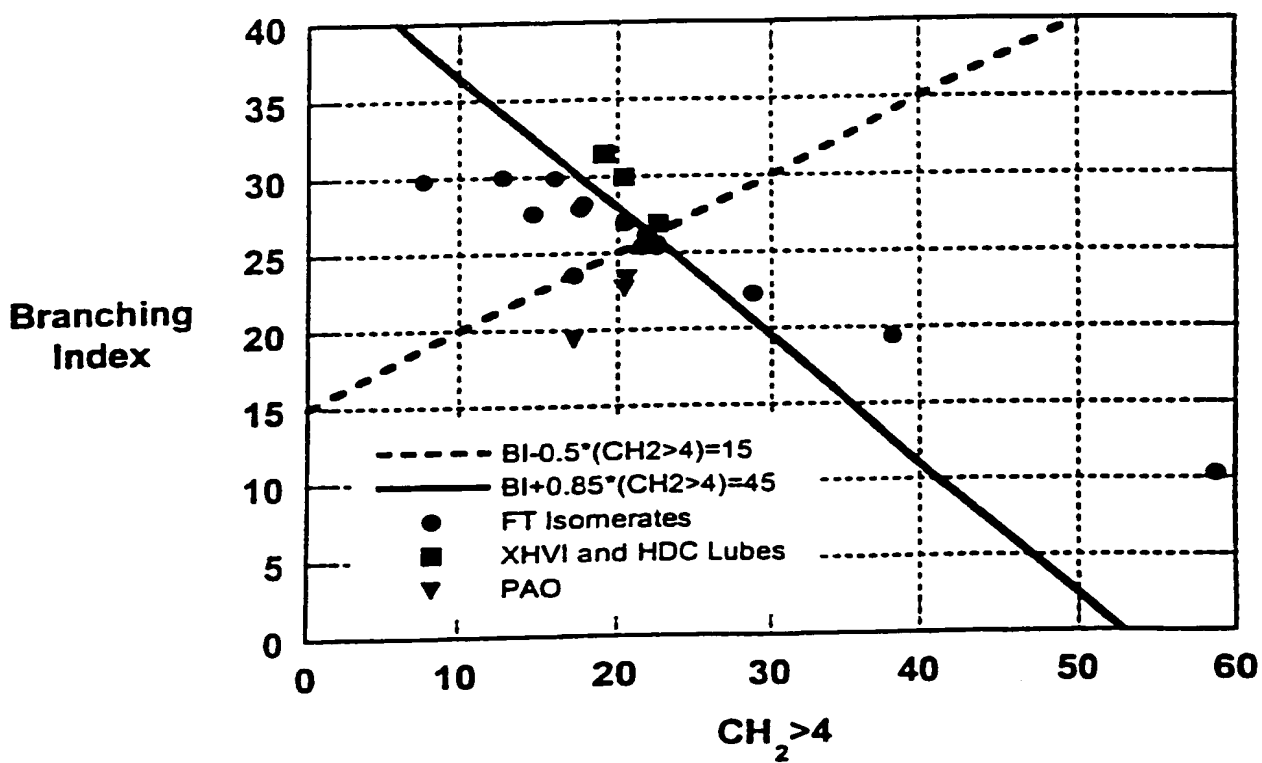
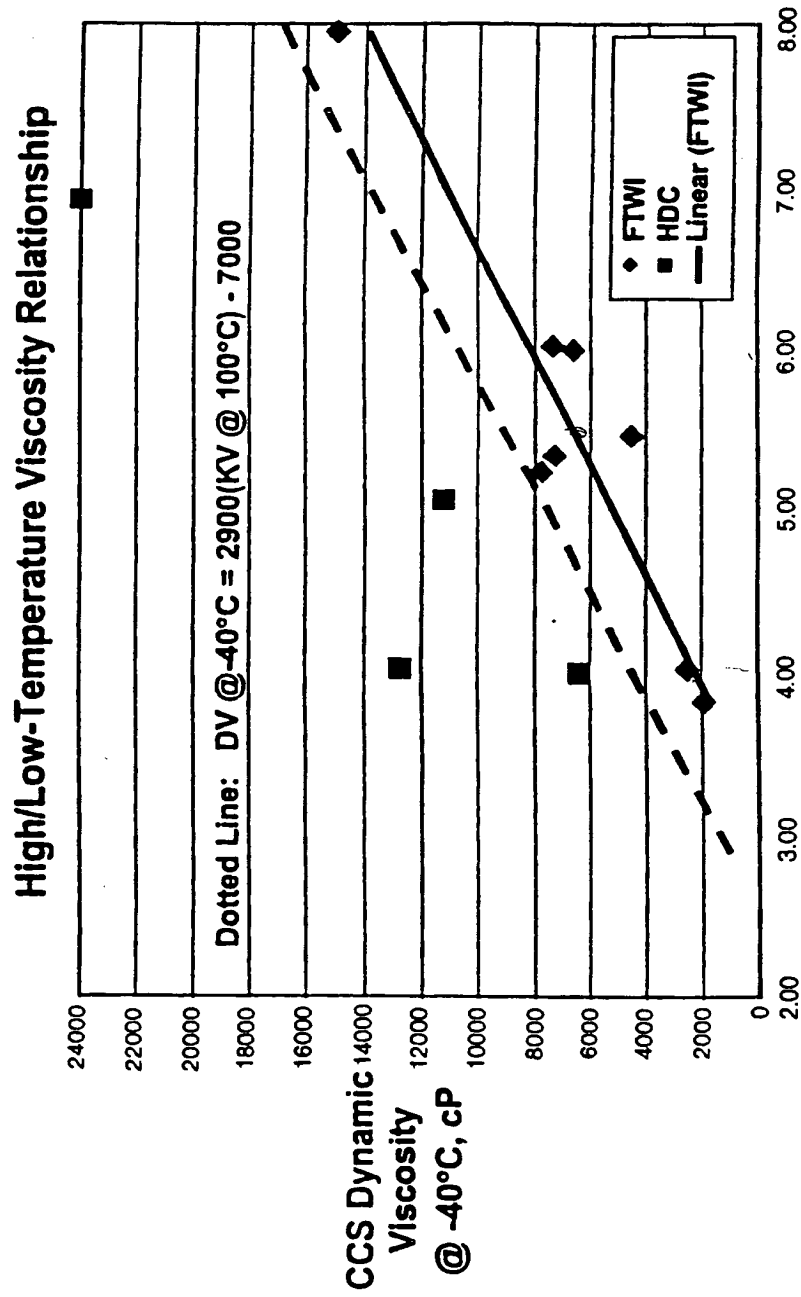


FIG. 2

3/4



Kinematic Viscosity @ 100°C, cSt

FIG. 3

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VI, Low-Temp Viscosities vs Pour Point  
(Wax Isomerates 6 cSt @ 100°C)

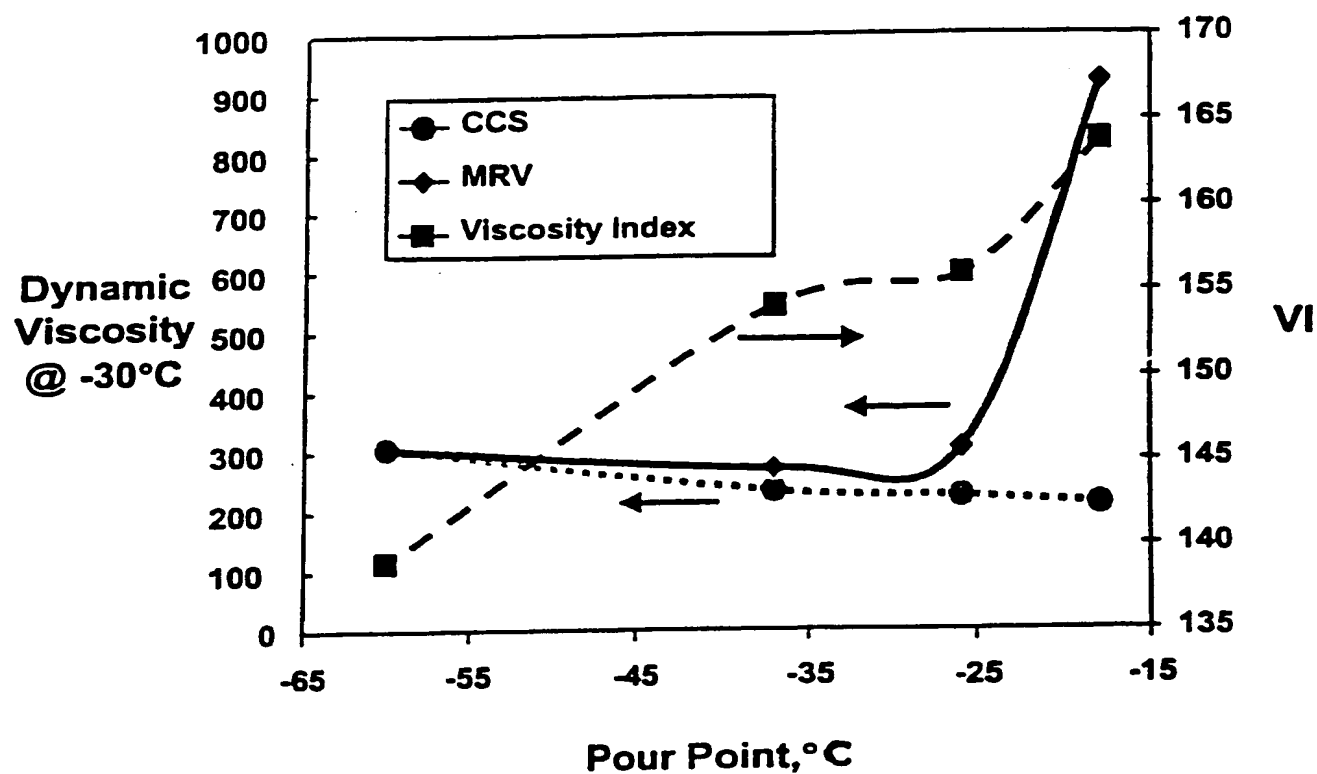


FIG. 4

## INTERNATIONAL SEARCH REPORT

International Application No

PC1/US 01/02645

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10M171/02 C10G65/12 C10M177/00 C10M169/04  
 //(C10M171/02, 105:04, 129:10, 133:12, C10M159:20, C10M159:22,  
 C10M159:24), C10N30:00, 30:02, 70:00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10M C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 20720 A (MOBIL OIL CORP) 29 April 1999 (1999-04-29) page 8, line 30 -page 9, line 29; claims 1-20; figures 1-3; examples 1-10 ---	1-36
A	WO 97 21788 A (EXXON RESEARCH ENGINEERING CO) 19 June 1997 (1997-06-19) cited in the application the whole document ---	1-36
X	WO 99 41332 A (EXXON RESEARCH ENGINEERING CO) 19 August 1999 (1999-08-19)  page 6, paragraph 2 -page 7, paragraph 4 page 14, paragraph 3; examples 1,2; tables 1-3 -----	1, 3-5, 11, 14, 21-26, 30, 35, 36



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

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Information on patent family members

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